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THE RAMAN EFFECT

and its

CHEMICAL APPLICATIONS

BY

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With a Theoretical Discussion

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THE GEORGE WASHINGTON UNIVERSITY



American Chemical Society
Monograph Series

BOOK DEPARTMENT

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To
LOUISE AND PHYLLISANN
I DEDICATE THIS BOOK

GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed editors (the present list of whom appears at the close of this introduction) to have charge of securing authors, and of considering critically the manuscripts submitted. The editors endeavor to select topics of current interest, and authors recognized as authorities in their respective fields.

The development of knowledge in all branches of science, especially in chemistry, has been so rapid during the last fifty years, and the fields covered by this development so varied that it is difficult for any individual to keep in touch with progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and by such compendia as Beilstein's *Handbuch der Organischen Chemie*, Richter's *Lexikon*, Ostwald's *Lehrbuch der Allgemeinen Chemie*, Abegg's and Gmelin-Kraut's *Handbuch der Anorganischen Chemie*, Moissan's *Traité de Chimie Minérale Générale*, Friend's and Mellor's *Textbooks of Inorganic Chemistry* and Heilbron's *Dictionary of Organic Compounds*, it often takes a great deal of time to coördinate

the knowledge on a given topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

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Preface

In March, 1928, in an inaugural address delivered to the South Indian Science Association at Bangalore, Sir C. V. Raman first announced the results of his observations and those of his associates, which have led to what has since been universally termed the Raman effect. This address, entitled *A New Radiation*, summarized the preliminary experimental work on scattering and fluorescence which ultimately led to the conception of a new type of secondary radiation considered as an "optical analogue of the Compton Effect."

This discovery, like any other in modern times, is not in the broad sense unique. Smekal previously had made reference to the interaction of light with molecules and it may be argued likewise that Lallemand in 1869 experimentally observed an equivalent phenomenon. Indeed in more modern times Landsberg and Mandelstam independently came to similar conclusions.

The fact remains, however, that beginning with the announcement by Raman this subject has been investigated in the laboratories of practically every nation in the world, with the result that within the last decade there have been over two thousand publications on the Raman effect. This widespread interest cannot be attributed solely to the newness of the discovery—inasmuch as there have been other discoveries within this decade—but primarily to its fundamental nature from both a physical and a chemical point of view. In view then of the more or less general applicability of this phenomenon, it is not strange that its impetus has been a considerable factor in the expansion of modern physics in the field of chemistry. -

The Raman effect itself, although essentially physical in nature, is another parameter by which the behavior of atoms within the molecules and of the molecules themselves may be determined independently of their state of aggregation. Applications of this effect have been made, therefore, to both physics and chemistry. Many of the chemical applications, however, which constitute the principal subject matter of this monograph, are independent of the physical mechanisms responsible for the Raman lines, and are useful to the extent to which they serve to explain the common facts of chemistry. These applications are based on empirical observations correlating observed Raman shifts with the constituent atoms and groups present in chemical compounds of known structure, and have yielded interesting and fruitful results concerning the constitution of organic and inor-

ganic compounds as gases, solids, liquids and in solutions. This empirical method results in a much wider application than would be obtainable from a strictly theoretical approach. The chemist, in general, has not had to appeal to wave mechanics to explain the precipitation of barium sulfate, for example, by means of a sulfate ion. This is generally accepted as a *fait accompli*. Likewise certain Raman shifts may be correlated with certain types of chemical binding, irrespective of their physical or mathematical history. While susceptible to modifications as new facts are accumulated, the purely empirical conclusions are now based on a sufficiently large number of results to contain more than an element of truth and to carry the same weight as any other experimentally determined facts. The interpretation of these observations, of course, like that of other statistical determinations, is a matter of opinion and can be viewed as correct only to the degree of reasonableness by which such interpretations account for the observed results.

The most interesting applications of this philosophy occur when the results, based on the Raman effect, are divergent from those obtained by other methods or when no other method yields reasonable conclusions. It is frequently assumed, for example, that common inorganic and organic substances have certain definite formulas. A perusal of the literature, however, shows that these assumptions are often a function of environment or interpretation. Through Raman spectra it can be demonstrated unequivocally that the classic assumptions, while correct in certain cases, are in others either incorrect or subject to modification.

Although application of Raman spectra to the more complicated molecules is based principally on experimental observations, theoretical principles apply of course to all molecules. The realization of a complete mathematical picture of the modes of vibration in these cases is not always possible. This difficulty, however, is not confined to Raman spectra. It occurs also in band spectra, infrared absorption and other physical problems of this nature.

On the other hand the number of simple molecules which can be dealt with completely on a theoretical basis is by no means negligible. Furthermore the vibrations of complicated molecules may be at least partially analyzed. Specific groups sometimes retain, as a first approximation, their individual vibrations and this is, of course, directly related to the success of the purely empirical approach. Of particular interest are the rules and conditions which must be satisfied, from a physical and structural point of view, before Raman lines will appear. In many cases this has been of great assistance in the delineation of chemical constitution. There are also laws governing the magnitude and kind of Raman lines, their degrees of depolarization and their intensities, all of which are in turn dependent on

the types of molecular vibration. All these factors represent the theoretical or physical contribution to the interpretation of chemical structure and will be treated in detail in the text.

It may be said that both theoretically and empirically Raman spectra have contributed in large measure to the understanding of molecular constitution and molecular behavior. It is the purpose of this publication to describe in detail how this has been accomplished. The treatment of this subject is divided into three parts: Part I deals with the nature of the Raman effect, its relation to other physical manifestations, and the vibrations and rotations of polyatomic molecules; Part II deals with the application of those principles to organic chemistry; Part III deals with their application to inorganic chemistry.

A final paragraph describing the order in which the material is presented in this monograph is advisable. There are several strictly logical arrangements possible for this material and each of these arrangements conflicts to a certain extent with the others. On this basis alone a purely logical arrangement is impossible, even if it were desirable, which is not the case. Consequently it has been decided to present the large mass of data in such a way as to emphasize the significant conclusions which can be drawn from it. The phosphates, for example, are placed under the Raman spectra of the acids, and the sulfates are treated separately. In the numerous cases where an individual substance might logically be treated in more than one place, it has been placed where it could be treated most effectively; in every such case cross references have been inserted in the text so that the reader will have no difficulty in locating the material.

Other sources of comprehensive information concerning Raman shifts are included as an introduction to the detailed bibliography.

The author wishes to express his great appreciation of the assistance of A. H. Blatt in the preliminary editing of this volume, to Donald Andrews for reviewing it in manuscript form, to Edward Teller for his coöperation in jointly writing part of it, to Thelma Barnard for her assistance in typing and preparing the manuscript, to G. G. Hawley for preparing the numerical index, and to his friends and colleagues in Washington who have generously given, from time to time, information, advice and criticism.

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Part I

A General Discussion of the Raman Effect: its Practice and its Theory

Chapter 1

The Nature of the Raman Effect

As has been stated in the Preface, the Raman effect is essentially another means by which the behavior of atoms in molecules may be measured independently of the state of aggregation. Other direct methods, such as x-ray and electron diffraction, have indicated the position of the heavier atoms. These methods, like the Raman effect itself, have certain limitations. Fortunately, as compared with the Raman effect, they are complementary in the sense that what one system lacks the other provides. The information obtainable from Raman spectra concerns the forces between the atoms in a molecule in its normal state, the arrangements of the atoms in space, and the amplitudes and frequencies of their vibrations. This leads in many cases to a determination of the specific type of chemical linkage which exists in a molecule and to the calculation of specific heats and other information of interest to the physicist and to the chemist.

Origin and Nature of the Raman Effect

Perhaps the best approach to the problem of the origin and nature of the Raman effect is an analogy between it and x-ray analysis, which is known to some extent by everyone. In the latter case the atoms in a given molecule are bombarded with radiation whose length is relatively short compared to the size of the molecule. The diffraction of this radiation is recorded on a photographic plate as definite spots which are a function of the interatomic distances. In Raman spectra a molecule is bombarded with radiation of wave-length much greater than the size of the molecule. The type or wave-length of light used, however, is in general immaterial. It may be of long wave-length, as represented by red light, or it may be of short wave-length, as represented by far ultraviolet. Using x-rays, one deals essentially with a static arrangement; with the Raman effect, one deals not with a static but with a dynamic situation. Here it is primarily a question of the motion of the atoms in the molecule and only indirectly of their position in space. Nevertheless, as will be seen later, the geometric distribution of atoms does influence the result.

In effect, therefore, molecules regardless of their state of aggregation are irradiated with light. These molecules may be in the liquid, solid or gaseous state. The light used is preferably monochromatic, that is, of a

single wave-length whose energy content is given by $h\nu$ where ν is the frequency and h is Planck's constant. When these quanta of energy, or photons, collide or interact with the molecule, part of the energy they represent may be distributed throughout the molecule in all its vibrational and rotational degrees of freedom. The results of this interaction appear in the light scattered by the molecules; and this, after being transmitted through a spectrograph and photographed on a plate, is recorded as definite spectral lines. If real monochromatic radiation is employed (which is very difficult to realize experimentally) it results in a single strong line on the photographic plate, corresponding to the incident radiation, plus other much weaker lines if definite amounts of energy have been subtracted from the original quantum. These weak lines are indirectly related to the different types of vibration and rotation which the atoms in the molecule possess. The net result of this process is the production or re-radiation of light of longer wave-lengths than exist in the original beam and which is emitted by the molecules themselves. This is closely related to two other physical phenomena, absorption and fluorescence, which should now be carefully differentiated from the Raman effect.

Relation to Absorption and Fluorescence

In absorption, the light energy, $h\nu$, is usually degraded to heat or electrical energy and is *directly* related to the vibration and rotation of the atoms in the molecule. If the quanta are re-emitted, this may be called fluorescence. This effect differs from the Raman effect and from Rayleigh scattering only in degree and not in fundamental principle. Fluorescence, unlike Raman spectra, may be excited only by light of well defined wave-lengths, namely, light which is absorbed by the fluorescent material. The light thus absorbed may be re-emitted at a longer wave-length or at the same wave-length. In the latter case this is termed resonance fluorescence. Light of shorter wave-length than the original radiation may also be emitted, but only if the absorbing molecule is already in a higher energy level than normal. In Raman spectra this is the anti-Stokes effect. Finally it may be stated that, as a rule in fluorescence, absorption and re-emission take place in measurable time, about 10^{-9} second, and are fairly efficient; in other words the amount of light re-emitted is of the same order as the absorption. Three qualitative differences between Raman spectra and fluorescence have thus been mentioned: the time required, absorption factors and the relative intensities of the two effects.

Rayleigh or ordinary light scattering from molecules or small particles is always present in the Raman effect. The appearance of the exciting radiation in the Raman spectra is due to Rayleigh scattering. This differs from fluorescence in that it is weak, instantaneous and qualitatively inde-

pendent of wave-lengths. The intensity of both Raman and Rayleigh scattering increases as the fourth power of the incident frequency except in the neighborhood of an absorption band, where the scattering intensity increases still more markedly. This behavior is due to the fact that the polarizability of the system depends on the frequency, and all scattering is a function of polarizability.

The distinctions between the Raman effect, absorption, fluorescence and Rayleigh scattering having been made, the Raman effect may be described as being feeble, instantaneous, independent of absorption, qualitatively—but not quantitatively—independent of the wave-length of the exciting radiation; and it results in the re-emission of light generally having a wave-length longer than the exciting one. The principal factor of interest in this process, however, is the *difference in wave-lengths or frequency* between the wave-lengths of each re-emitted spectral line, or Raman line, and the wave-length of the incident or exciting radiation*. If these differences are expressed in frequencies rather than in wave-lengths, they may correspond directly—as in absorption—to the frequencies of vibration and rotation of the atoms within the molecule. The net result, then, is that the information obtainable from the Raman effect is somewhat analogous to that obtained by absorption, but in the Raman effect no absorption is involved. In actual practice the observed frequency differences represent wave-lengths in the infrared portion of the spectrum and are, on occasion, identical with known infrared absorption bands. The foregoing discussion represents only a rough description of the actual facts. It will be seen later that infrared absorption occurs only when there is a change in the electric moment of the molecule, and the Raman effect when there is a change in polarizability; and that the vibrations which are unsymmetrical with reference to the symmetry axes of the molecule usually appear strongest in absorption, and the symmetrical vibrations strongest in the Raman effect. Furthermore absorption bands and spectral lines may appear which do not represent vibrations of the atoms in the molecule but overtones and combinations of vibrations.

Polarizability

The relation between the Raman effect and the polarizability mentioned above is discussed in some detail in Chapter 4. However, it is pertinent to this preliminary survey to mention, first of all, that the theory of all scattering phenomena is based on the fact that light consists of electromagnetic waves, or of short oscillating electric and magnetic forces. The oscillating electric field induces a dipole moment in the molecules which will in turn radiate light of the same frequency as the incident radiation,

* $\lambda\nu = c$, or wave-length $\times$ frequency = velocity of light.

but in different directions from the original source of illumination, and scattering results. The dipole moment is related to the electric force in the incident radiation by the following equation in which the two vectors are temporarily assumed to be parallel:

$$(1) \quad \vec{M} = \alpha \vec{E}$$

where α represents the polarizability, M the dipole moment and E the electric vector. If $\vec{E}_m$ is the amplitude with which the electric vector in the incident beam is vibrating, this is related to E as a function of time, by the following:

$$(2) \quad \vec{E} = \vec{E}_m \cos 2\pi\nu t$$

and the electric moment $\vec{M}$ induced in the molecule will have the value:

$$(3) \quad \vec{M} = \alpha \vec{E}_m \cos 2\pi\nu t$$

If it is assumed for the sake of convenience that all the atoms in the molecule vibrate in the same phase with a frequency ν_0 the polarizability will change with the molecular configuration. If the atoms execute a periodic motion, α will change in a periodic manner and one may write:

$$(4) \quad \alpha = \alpha_0 + \alpha_1 \cos 2\pi\nu_0 t$$

where α_0 is the polarizability in the equilibrium configuration of the atoms; and α_1 the change of polarizability at the moment in which the atoms in the molecule have their maximum elongation. Substituting (4) in (3) leads to the expression:

$$(5) \quad \vec{M} = (\alpha_0 + \alpha_1 \cos 2\pi\nu_0 t) (\vec{E}_m \cos 2\pi\nu t)$$

the physical content of which is that the electric moment induced can be considered as arising from the superposition of three periodically changing moments having the appropriate frequencies ν , $(\nu + \nu_0)$ and $(\nu - \nu_0)$. These radiate light of corresponding frequencies and hence yield values corresponding to the Rayleigh line, the anti-Stokes lines and Stokes lines respectively as observed in the Raman effect.

Vibrations and Constitution

Before proceeding with a discussion of any relationship between the Raman effect and its chemical and mechanical aspects, it is necessary to adopt a system to describe the Raman lines in addition to their wavelength or frequencies. This will be discussed in detail at the end of the next chapter. However, for the present, it will be mentioned that by common convention or tacit agreement Raman effect results are reported

in terms of wave numbers per centimeter, or the number of vibrations per centimeter, usually abbreviated $\Delta\tilde{\nu}$,* to indicate that the Raman effect results are expressed as a difference between two quantities. The actual values may vary from $\Delta\tilde{\nu}$ 50 to near $\Delta\tilde{\nu}$ 4400.

If the factors which determine Raman lines on a numerical basis are known, the next question is, How are these lines specifically correlated with the information regarding the modes of vibration of the atoms in the molecule, the forces between the atoms, the structural representation of the molecule, and other fundamental information? This will be treated in detail in Chapters 3 to 7. For the moment there are some simple relations which, while they are crude and at best represent only an approximation in most cases, serve a useful purpose.

✓ In a simple molecule consisting of but two atoms vibrating against each other it can be stated with a fair degree of accuracy that the mechanical equation relating the frequency of vibration exerted between them is given by the well-known equation for a harmonic oscillation,

$$(6) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

where ν represents the frequency, k the force constant and m the mass. In an atomic system this will become

$$(7) \quad \Delta\tilde{\nu} = 4.125 \sqrt{\frac{k}{\mu}}$$

where μ represents the reduced mass, that is $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$, in which m_1 and m_2 represent the masses in terms of relative atomic weights of the vibrating components, $\Delta\tilde{\nu}$ is given in wave numbers per centimeter and k is the force constant in dynes per centimeter of displacement. The value 4.125 is derived from the conversion factor $\frac{\sqrt{N}}{2\pi c}$, where N is Avogadro's number and c the velocity of light in centimeters per second.

Thus a fundamental mechanical vibrational frequency in which all the atoms of the molecule participate may correspond to a vibrational Raman line.

The relative motions of the atoms with respect to each other, together with the forces exerted between them and their masses, determine the frequency of this vibration or the magnitude of the resulting $\Delta\tilde{\nu}$ shift. Except in the case of a diatomic molecule it is not entirely accurate to state, therefore, that a particular Raman line corresponds to a single type of linkage such as C—H. However, in any given molecule there is usually

*Also sometimes written $\Delta\nu$. In this book however Raman shifts will always be indicated by $\Delta\tilde{\nu}$.

some frequency originating in a vibration which consists chiefly of the linear or deformation oscillations in unison of atoms in particular groups. In ethylene, for example, there is one frequency which corresponds to the movement of the two CH₂-groups toward and away from each other. In this case the hydrogen atoms are moving in roughly the same direction as the carbon atoms. As their masses affect but little the C=C vibration—particularly since their motion is in phase with this oscillation—the net result is a characteristic frequency for the ethylenic linkage. In similar fashion, there is possible a motion of the hydrogen atoms toward and away from each carbon atom along the direction of the valence bonds, which gives rise to a frequency termed characteristic of this type of C—H

Table 1. Valence Forces (*k*) for Different Types of Linkage

Linkage	Frequency	<i>k</i> × 10 ⁻⁸ dynes cm ⁻¹
C—H*	3050	5.02
C—C	1993	4.64
C—O	1030	5.00
C—N	1033	4.85
N—H	3370	6.20
O—H	3650	6.80
H—H	4158	5.05
Cl—H	2880	4.75
Br—H	2558	3.80
S—H	2572	3.78
C—S	650	2.14
C=C	1620	10.60
C=O	1700	11.60
O=O	1556	11.40
C=N	1650	10.40
C≡C	2120	15.82
C≡N	2150	17.50
C≡O	2146	18.50
N≡O	2224	20.90

*Aromatic

linkage. Consequently, the characteristic frequencies and the force constants for various types of oscillation and bending may be determined. This is particularly valuable; first, because the presence or absence of a type of linkage may thus possibly be established and, secondly, because these frequencies are slightly altered by the proximity of other groups whose masses or effect on the valence force result in an alteration of the characteristic frequency. This is helpful in the delineation of the structure of the molecule.

Unfortunately, the number of Raman lines which can be elicited from a molecule is not confined to fundamental vibrations, that is, vibrations corresponding to a particular type of motion. Other lines may appear due to overtones (harmonics) of a given frequency or due to combinations. The latter may appear as sums or differences of other frequencies, with the result that in some cases there are nearly ten times as many lines as there are fundamental vibrations. These overtones and combinations usually have much less intensity than the fundamentals. For this reason, and because the numerical values and the degree of depolarizations of the combinations and overtones bear a definite relationship to the fundamentals, it is sometimes possible to make proper assignments of Raman lines even in complicated molecules where a profusion of lines appears in the same neighborhood. Otherwise it would be very difficult to state in other than general terms that a given line is due to any particular mode of oscillation. Some typical examples of characteristic frequencies and force constants for specific linkages are given in Table 1.

Of course some of these values are a function of what is accepted as the reduced mass. Nevertheless in a broad sense they represent general trends and indicate the change in force constant with the type of binding.

There are other relationships of interest involved in a diatomic molecule. One of these is that

$$(8) \quad \bar{a} = \sqrt{\frac{hN}{2\pi^2c}} \cdot \sqrt{\frac{1}{\Delta\tilde{\nu}\mu}}$$

where $\bar{a}$ is the greatest amplitude of the zero point vibration, c is the velocity of light, h is Planck's constant and N is Avogadro's number.

Then again in molecules of the type X_3 a ratio of two of the Raman frequencies becomes $\frac{\Delta\tilde{\nu}_1}{\Delta\tilde{\nu}_2} \approx \sqrt{2}$; in linear molecules of the type AX_2 , $\frac{\Delta\tilde{\nu}_2}{\Delta\tilde{\nu}_1} \approx \sqrt{\frac{M+2m}{M}}$; and in molecules of the type X_4 the ratio of frequencies should approximate $1:\sqrt{2}:2$.

Another relationship which has been employed to determine the valence angle in triatomic molecules is

$$(9) \quad \cos \alpha = \frac{M+m}{M} \cdot \frac{\Delta\tilde{\nu}_2^2 - \Delta\tilde{\nu}_1^2}{\Delta\tilde{\nu}_2^2 + \Delta\tilde{\nu}_1^2}$$

This and the other formulas given, are approximate and are applicable only under special conditions. These will be discussed more precisely in the succeeding chapters on the vibrations of polyatomic molecules.

There are two principal assumptions used in evaluating the force constants and frequencies in more complicated molecules. These are known as the *valence force system* and the *central force system*. Each system is

applicable to certain types of molecules. Both methods of calculating the vibrational frequencies in molecules have been sufficiently fruitful to indicate their general applicability provided the molecule is not too complex. Recently Wilson^{1691, 1692, 1693} has treated the problem analytically by means of the group theory. The frequencies calculated from these formulas are, in many cases, in reasonable accord with the experimental observations.

Conversely, the molecular configuration necessary to give rise to the correct number and distribution of Raman lines can likewise be determined. This involves a different method of approach, namely, the mechanical models of Kettering and Andrews and their co-workers^{58, 808, 1537} Trenkler^{1576, 1577} and Reitz,¹³⁰⁴ which simulate the vibration of atoms in molecules and give rise to frequencies of vibrations in fair agreement, in some cases, with observed Raman shifts. Wilson* has used a different type of mechanical analysis which has the advantage of being more flexible.

Lack of agreement between either the mathematical or the mechanical approach and the experimental observations is due primarily to mathematical or mechanical over-simplification. The application of mechanical models, however, is restricted largely to the study of certain relatively simple and stable types of vibration. Nevertheless, they indicate the realistic nature of the Raman effect and have a very useful purpose.

The discussion so far has been confined principally to the magnitude of the Raman shifts. 'In addition, the intensities and the degree of polarization of the Raman lines furnish information about the types of vibration.' For example, the vibrations which are symmetrical to the axis or center of symmetry of the molecule are usually the more intense and are polarized.¹ By taking into consideration these two factors it is much less difficult to assign a given Raman line to a specific type of interatomic vibration. A third aid in the interpretation of the Raman spectra and consequent delineation of the molecular constitution of the molecules is the use of isotopic substitution. The vibrations of hydrogen-d, or deuterium, are strongly affected by the increased mass, and it is possible to separate from the entire spectrum those lines which can be ascribed to hydrogen vibrations by comparing the spectra of the hydrogen compounds with those of the corresponding deuterium compounds.

The theoretical treatment of all these factors, namely, the vibrations of polyatomic molecules, the nature of the Raman effect, infrared absorption, symmetry, polarization and other interrelated physical manifestations is given in more detail in subsequent chapters. The treatment given in this chapter, it must be emphasized, is purely descriptive and the processes have been much over-simplified.

* A.C.S. meeting, Rochester, N. Y., 1937.

Chapter 2

Experimental Methods and Definitions of Terms

Spectrographic Equipment

The actual spectrographic arrangement employed in determination of the Raman effect will be made clearer by means of a diagrammatic illustration of the apparatus used and by a picture of the Raman lines as they appear on the photographic plate. These are shown in Figures 1 and 2.

The spectrograph itself may be of the simplest possible design, for example, made with fixed prisms and without wave-length scale. It is necessary, however, to have good resolution, reasonable dispersion and high speed. The *effective* aperture should not be greater than F:10 and should approach F:3 to F:6 if possible. In the spectral region used for excitation the dispersion, if possible, should be better than 35 Ångströms per millimeter. A much greater dispersion would be advisable. The choice between a quartz spectrograph and a glass one depends on the materials to be investigated. As will be discussed later, the higher the exciting frequency the more intense are the Raman lines. In consequence of this it is advantageous to use a spectrograph permitting ultraviolet excitation. However, this advantage may be offset or entirely cancelled if the material to be irradiated absorbs in the spectral region used for excitation. There is no object in using quartz substitutes which will transmit only in the near ultraviolet.

With a quartz spectrograph having an aperture of F:6 and using λ 2537 for excitation, a Raman spectrum of methyl alcohol, for example, may be obtained in five minutes. It would take approximately four hours to record the same spectrum with a glass spectrograph having an aperture of F:10 and using λ 4358 for excitation. In the case of water the ratio would be one-half hour as compared with 24 hours. If filters are used in the visible spectral region—as will be discussed later—the comparison may easily be one-half an hour's exposure on the one hand and five or six days on the other. The extremely long exposures are limited by practical convenience, temperature changes in the optical system, vibration of the spectrograph and stray light.

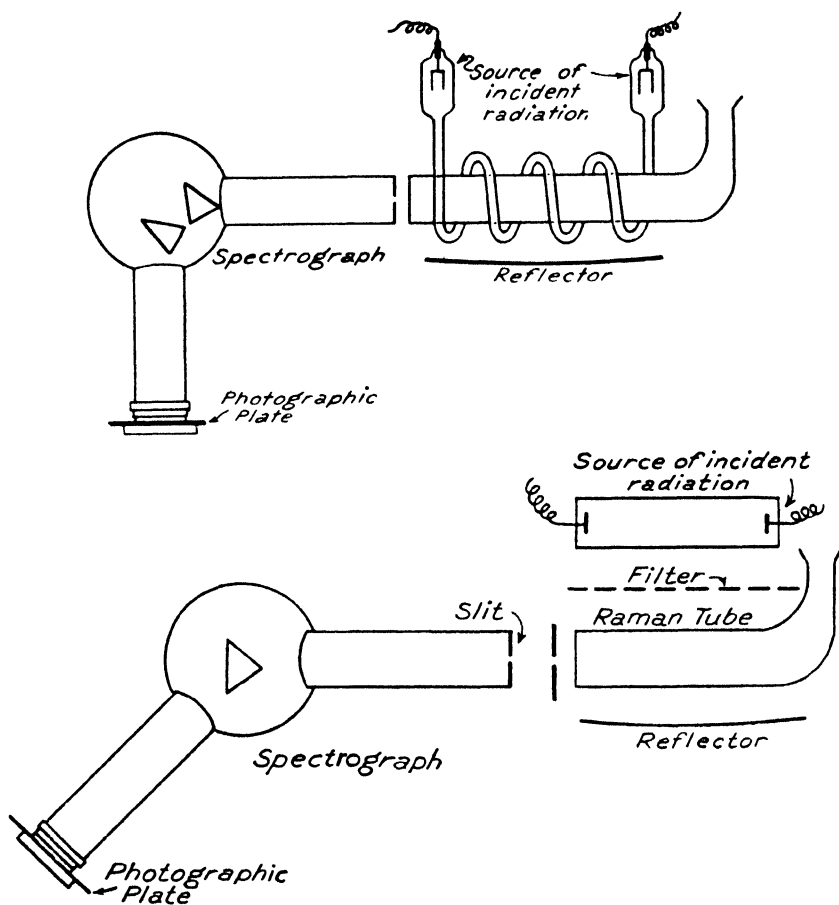


FIGURE 1. Experimental Arrangements for Recording Raman Spectra.

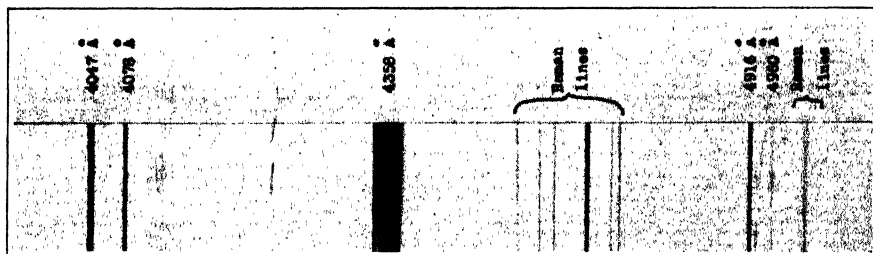


FIGURE 2. The Partial Raman Spectra of Nitrobenzene Excited by the 4358 Å Mercury Line.

Methods of Illumination

The source of light illustrated in the first figure is generally a mercury arc. This type of arc has four lines, among many others, which are sufficiently intense and reasonably well separated from other lines to be useful for this purpose. These lines, which do not all appear in the figure, are 2537, 4047, 4358 and 5461 Å units. After the selection, therefore, of a given wave-length to be employed to excite the Raman lines, the experimental set-up is so arranged that this radiation or light will pass through the material to be studied and at right angles to the end of the spectrograph. This serves to diminish as much as possible any direct light from the lamp striking the opening of the spectrograph. The only light desired is that which comes from the molecules being investigated. Unfortunately, a spectrograph can also "see" the light which is scattered from these same molecules in the form of Rayleigh scattering. Neglecting polarization, this light is identical with the original exciting radiation. The net result of these two scattering phenomena is therefore a series of lines consisting of the intense line corresponding to the original source of radiation and the less intense Raman lines which were not present in the original light.

Since a complete series of Raman lines appears for *each* exciting or incident radiation, it is highly essential that the incident light be monochromatic. The modified lines or Raman lines are all extremely weak as compared to the original source of excitation, so that it is also important to have great intensities of exciting light and efficient optical systems. It is in these directions—namely, toward monochromatism and adequate intensities—that the major developments in technique have taken place.

Lamps

The most common source of light is the mercury arc; the helium lamps suggested by Wood^{1701, 1706, 1707} are more or less impracticable except in special instances. The mercury arc provides three lines of importance, the 4358, 4047, and the 2537 Å lines. The use of the 4358 Å is quite general, but its utility depends on the elimination of the 4047 Å as a simultaneous source of energy. Throughout this book emitted lines from the source of excitation will frequently be referred to as λ 2537, λ 4047 and so forth.

Perhaps the principal single advance in technique that has taken place in recent years is the use of the low-pressure and low-current silica mercury arc. This arc operates in conjunction with a high-reactance transformer which supplies about 2000 volts as a starting voltage and drops to near 400 volts or less as an operating voltage, depending on the length

of the tube. These tubes may be made in any shape or form. Helicoidal models containing 9 feet or more of 5-mm. tubing have been used. The discharge is maintained by means of a small quantity of inert gas which does not contribute emission lines in the ultraviolet region. This type of lamp has the advantage of providing a strong λ 2537 line for excitation purposes which is not reversed by a layer of mercury vapor near the walls. In consequence of this, the actual intensity of the λ 2537 line in a lamp operating on 150 milliamperes is greater than in the high-pressure type operating on 7 amperes. Furthermore 85 per cent of the total energy is confined to the λ 2537 line.

There are some disadvantages to this lamp. These are chiefly the interference of λ 2576, 2603, 2640, 2650-53, 2699, 2753 and 2759. In general this interference is only serious in the $\Delta\bar{\nu}$ 3300-3600 region. Related disadvantages are the necessity of using a quartz spectrograph and the fact that studies are restricted to those compounds which will transmit in the ultraviolet.

The overall gain is a more efficient irradiating system through the use of long tubes of various shapes and the fact that the intensity of the Raman effect increases as λ^4 decreases. In other words, λ 2500 is 16 times as effective as λ 5000.

To increase the intensity of light used for special excitation purposes, lamps other than mercury arcs and especially designed mercury lamps have been employed. Krishnamurti⁹⁰⁹ used a cadmium arc¹⁰⁶ containing 50 per cent tin, although a small amount of gallium may be used to replace the tin. This gave as exciting lines λ 4800, λ 5086, and λ 6438. A simple capillary fused silica mercury lamp has been described by Daniels and Heidt.⁴⁵² Lamps similarly constructed but developed to use metals other than mercury, such as bismuth, cadmium, lead, thallium and zinc, have been constructed by Hoffman and Daniels.⁷⁴⁷ A special mercury lamp designed with a discharge surrounding the material to be investigated is described by Venkatesachar and Sibaiya.¹⁰⁰⁶ This is similar to the lamp previously developed by Bates for photochemical studies. A spiral mercury lamp for the study of crystals has been developed by Hibben. A hot-cathode helium lamp in a reflecting apparatus, so arranged that the Raman tube is at one of the foci of the ellipse and the helium lamp at the other, has been described by Buttolph⁸⁰⁵ and a reflecting device made from automobile headlights is discussed by Pfund.¹²³⁰ A system of illumination characterized by the placing of a number of vertical glass mercury lamps symmetrically around the Raman tube and within parabolic reflectors has been used by a number of workers.

Filters

Failure to eliminate the λ 4047 line completely if the λ 4358 is used as a source of excitation leads to discordant results. The same is true of λ 4358 if the λ 4047 line is the exciting one. In addition to these difficulties the continuous spectrum emitted by the mercury arc must likewise be diminished. The standard filter for the removal of the λ 4047 line has been an acid solution of quinine sulfate which, however, has the disadvantage of decomposing on prolonged exposures. Pfund¹²²⁰ found that a 12-mm. layer of a saturated solution of sodium nitrite transmits 65 per cent of the λ 4358 mercury line and only 1 per cent of the λ 4047 line. Likewise, *m*-dinitrobenzene^{93, 744} transmits the greater portion of the λ 4358 and little of the λ 4047 line. A combination of Corning Noviol A and Blue Purple Ultra glasses isolates, to a degree, the λ 4358 Hg line. A picric acid solution may be used to dye an unexposed and fixed photographic film. These films serve as filters of various shapes to reduce the intensity of λ 4047. A cobaltithiocyanate solution will diminish the background between λ 4358 and 5461. Amy and Poremsky¹⁶ recommend a 6-per cent solution of nitrobenzene and 0.5 gram of rhodamine 5G extracted with 100 cc. of alcohol at 96°. The filter absorbs 60 per cent of the intensity of the λ 4047 line although it may be remarked that nickel nitrate solutions are more efficient than this. It must be frankly admitted that there is no perfect system and any monochromatic gains are at the sacrifice of some intensity. Krishnamurti⁹¹¹ has suggested sodium salts of *o*-cresolphthalein, and West and Farnsworth¹⁶⁸¹ *p*-nitrotoluene for the isolation of the λ 4047 mercury line. Corning Red Purple Ultra glass is about as efficacious for this purpose as any filter. For the isolation of the λ 2536 mercury line, Bolla¹⁹⁰ used a mercury-vapor filter to prevent halation, and Hulubei⁷⁷⁰ used chlorine under pressure. The use of Corning glass Noviol O to eliminate the λ 3650 mercury lines, concentrated praesodymium solutions to eliminate some of the halation from the λ 4358 mercury line, and a solution of iodine and carbon tetrachloride as a filter to reduce the λ 4358 mercury line, in favor of the λ 4047 mercury line, as well as various optical arrangements, have been suggested by Wood.^{1709, 1711, 1712} Amy¹⁵ has suggested other glass filters.

Optical Systems

To obtain much greater increases in effective intensity, efficient optical systems are necessary. These have been discussed by Anand,^{17, 18} Almasy,⁹ Grassman,⁶³⁷ and Mesnage.¹⁰⁸⁷ The filling up of the spectrogram with light has been considered as a geometrical problem by Nielsen.¹¹⁶⁹ Other improvements have been suggested by Hulubei and Cauchois^{771, 772} and by Ziemecki.¹⁷⁵²

Inhomogeneous Solids, Fluorescent and Colored Liquids

One of the early studies of crystals was made by Landsberg and Mandelstam.⁹⁴³ This consisted essentially of illuminating the crystals with a mercury lamp the image of which is focused on the object by means of a condensing lens, the spectrograph being placed at the same time at right angles to the direction of illumination. As large crystals are rare it became necessary to develop a technique for the study of small crystal aggregates and inhomogeneous solids. Bär,⁸⁹ Menzies,¹⁰⁸⁰ Gerlach,⁵⁹² Krishnamurti⁹⁰⁵ and Hibben⁷²⁹ have devised special methods for illuminating crystals so as to reduce the amount of Rayleigh scattering. Hibben has also added a liquid of approximately the same index of refraction as the crystals being studied, as as to reduce the general scattering, and has interposed a mechanical filter in front of the photographic plate to keep the exciting line from striking it, thus preventing a spreading of the halation. Ananthakrishnan²⁴ has employed to advantage various filters to absorb the exciting radiation. These are placed in front of the slit of the spectroscope, but they have the disadvantage common to all such filters of partially absorbing in the region where transmission is desired. A crystalline powder method using two spectrographs with a common slit is supposed to yield good results.³⁸¹ Most of these methods are reviewed by Kohlrausch.⁸¹⁹

Fluorescence of either the impurities in a liquid or the liquid itself is a disadvantage to any Raman spectra measurements. The fluorescent bands are likely to appear in the region of the spectrum where the Raman lines occur. This condition may be ameliorated by filtering out all light having a wave-length shorter than the exciting one. Frequently the fluorescence results from photochemical decomposition products. These can be eliminated by using a constant circulating device such as that employed by Pal and Sen Gupta.¹²⁰⁴ Another means of reducing fluorescence has been employed by Hibben.^{728, 730} This consists of adding a small percentage of potassium iodide or nitrobenzene to the solution, thus quenching the fluorescence by collisions of the "second kind."

Colored liquids or solids are undesirable sources of Raman lines if they can be avoided. The exciting radiation must be transmitted freely by the material being investigated. As the possible long wave-length sources of excitation are limited to λ 5461 and 5890, this means the substance irradiated cannot be colored more than a pronounced yellow.

Measurement of Raman Lines

Since Raman shifts represent a difference between the number of waves per centimeter, or the wave number of the Raman lines, and the wave number of the exciting line, it is necessary to know the exact wave-length

(in Ångström units) of the Raman line. This is related to the wave number by the following:

$$(10) \quad \lambda A = \frac{10^8}{\tilde{\nu}}$$

where $\tilde{\nu}$ is in wave numbers per centimeter. This wave-length can be determined either by interpolation between known lines of the exciting source using the Hartmann dispersion formula, or by superposition of known lines of a standard iron or copper arc on part of the Raman spectrum. The latter is the more accurate method.

Measurements of the position of the Raman lines with reference either to the exciting lines or to iron standard lines may be made by means of a comparator or by projection. The former is better when the lines are weak, or broad and diffuse.

A system of projection and measurement is shown in the accompanying figure.

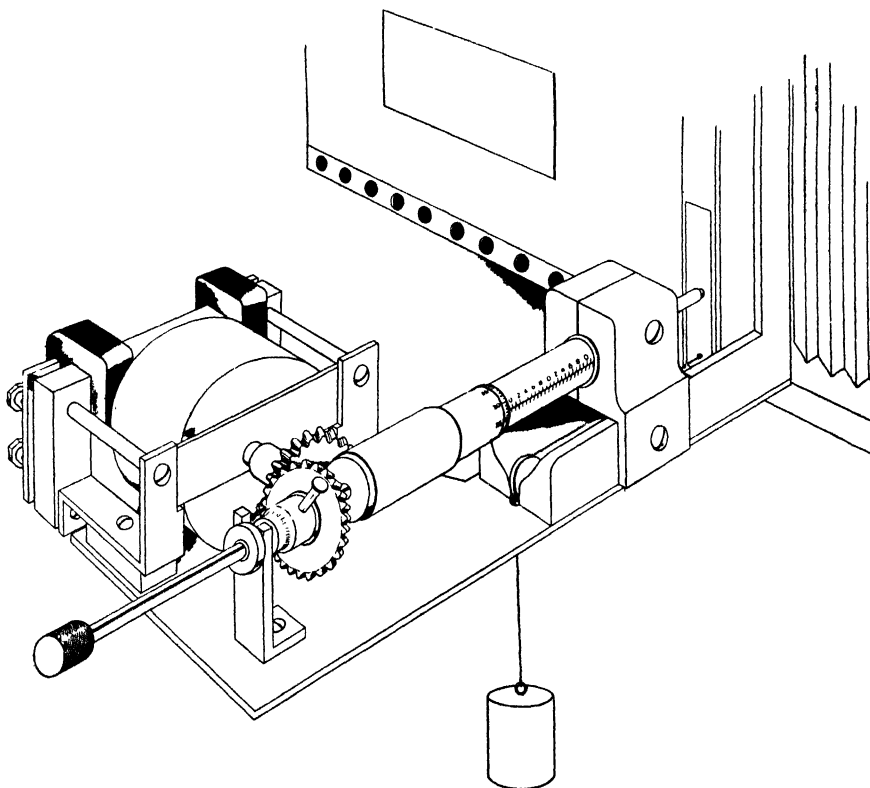


FIGURE 3. A System of Wave-length Measurement by Projection.

The projection lantern is an ordinary type, but in front of the objective lens is placed a plano-cylindrical lens. This serves the purpose of diminishing the grain effect. A micrometer, driven by a reversible synchronous motor, moves the plate-holder across the focal plane of the projection lens. The image of the Raman spectra is projected onto a flashed-opal screen in front of which is stretched, vertically, a fine tungsten wire for the zero line, and behind which the investigator may make the observations. As the plate is moved, the image of the Raman lines traverses the zero line and the observer can read the distance moved directly from the micrometer by means of a magnifying glass placed in front of it. This makes a system independent of the optics. Measurements can be made with an accuracy greater than 0.01 mm. and the magnification is sufficient to examine a small portion of a broad line without fatigue. Most important of all is the fact that very faint lines are not only visible but measurable when they are too feeble to be located with a comparator. An added refinement is the introduction of a thick glass plate just in front of the opal-glass screen in such a position that it is penetrated by one-half of the horizontally projected Raman spectrum image. As this glass plate is swiveled away from the screen the bottom half of the Raman lines is diffracted, thus sensibly moving this portion to one side without moving the plate, and permitting a closer setting of the zero line at the center of a Raman line. While projection methods are not new this particular system is more suitable than the usual ones.

Another method of measurement may be resorted to in particular cases. A microphotometer tracing of the Raman lines or bands is made on a photographic film. This film is then superimposed on a spectrum of an iron arc which has been made by hand from a similar tracing of an iron arc spectrum. Interpolation between the comparison spectral lines and the peaks of the microphotometer tracings can be made by the usual methods. The use of film in this connection avoids unnecessary expansion and contraction of the recording base. The supreme advantage of this method is the ability to measure the maxima of bands as determined by microphotometric means.

Special Apparatus

A special apparatus for studying the Raman effect in liquids at liquid air temperatures has been described by McLennan, Smith, and Wilhelm,¹⁰⁵³ Sutherland,¹⁵²³ Daure,^{456, 457} Epstein and Steiner,⁵³⁵ and Glockler and Renfrew. Typical apparatus used for the investigation of the Raman effect in gases under pressure has been designed by Bhagavantam¹³⁸ and Rasetti.¹³³²

A method of illumination with minimum reflection losses has been devised. This is a central Raman tube surrounded by two other glass-

walled vessels constructed in a manner similar to a three-walled Dewar flask, sealed at both ends, with individual and separate methods of filling. For example, one layer surrounding the Raman tube may be filled with sodium nitrite solution and the other with cobaltisulfocyanide solution; the combination acts as an effective filter to isolate the λ 4358 mercury line. This system keeps the liquid to be investigated at an even temperature, is optically efficient, and provides better absorption characteristics than do glass filters. The detrimental effect of plate grain on the visibility of spectral lines is diminished by oscillating the plate parallel to the lines and in the plane of the plate.¹⁹⁵

Kudryavtzeva⁹⁻⁹ has employed a photoelectric counter in place of plates to study Raman spectra. This offers very interesting possibilities.

Special Methods

Prosard and Bhattacharya¹²⁶⁰ have calculated the Raman shifts in a number of glasses and in some organic and inorganic solutions by means of "optical catalyzers." In these examples, where an absorption band in the visible spectrum is lacking, it is introduced by means of the addition of a solute to a solution—or by means of another component in the case of the glasses—which show absorption in the visible regions. The material is then irradiated and the maxima of the fluorescent bands determined. The maxima of the absorption band are considered to be the incident exciting radiation and the maxima of the fluorescent bands as the Raman lines. It is claimed that this method yields results in shorter time and that faint lines can be brought out with greater ease. This concept is supported by Hartley⁷⁰⁰ on theoretical grounds. From an experimental point of view, however, these claims have not been substantiated by the work of others.

Plates

The choice of plates depends primarily on the speed of the spectrograph and the weakness of the Raman lines. If the spectrograph has an effective aperture of from $F:4$ to $F:6$ a slower and finer-grained plate may be used. This is of particular value when microphotometer tracings are to be made. If the exciting radiation is λ 2537 a medium-speed and medium-grained plate not specially sensitized to the ultraviolet may be used. In the visible spectrum the Raman lines will generally appear between λ 4000 and 5100 or in the region requiring no special color sensitivity. In this spectral region the highest-speed plate obtainable is usually necessary even at a sacrifice of small grain. The backing of plates to prevent halation is not only desirable but in some cases is indispensable. In development a contrast developer gives best results.

Intensities

The relative intensities of Raman lines are as important as their degrees of depolarization. In the very early days of Raman spectra investigations, estimates of intensity rarely were given. During the last six or seven years, however, it has become common practice to report the Raman lines as strong to very weak, or on a ten to zero numerical basis. In this volume all intensities, where such data are available, are given on the numerical scale regardless of the system employed by the *original* author. This may seem somewhat arbitrary but it disposes of a complicated mixture of several methods and results in no more inaccuracy than that included in the original estimates.

There are but two practical methods of determining the intensities of Raman lines. One is by visual estimate or comparison and the other by means of a microphotometer tracing. Usually comparisons are made in terms of the degree of blackening of the weakest lines on a given plate as compared with the strongest one.

If a comparison is made between two different substances on two different plates, then the time of exposure necessary to bring the strongest line of the weaker spectrum up to the intensity of the most intense lines in the other spectrum must be taken into consideration. Errors are, of course, introduced by different types of development and by the use of plates having a different gamma. Notwithstanding the crudity of this method, surprisingly, reproducible results are obtainable by visual estimation. This is an art, however, rather than a science and requires cultivation.

Microphotometric tracings of the Raman plates are, of course, more accurate than any visual method. However, errors may still occur from development, exposure and plate gamma. If there is a strong background scattering the vertical heights of the line no longer bear any simple relationship to the actual intensity. 'The microphotometer method is of particular advantage where broad bands are being considered, for the maxima of these bands can be determined with accuracy.'

Polarization

In addition to the magnitude of Raman frequency shifts, that is, the differences in wave numbers between the exciting radiation and the Raman lines, there are two other parameters or coördinates of nearly equal interest. These are the polarization of Raman lines and their intensities. One of the most satisfactory of the earlier methods devised to measure polarization has been described by Cabannes and Rousset³⁸⁰. These authors have pointed out the well-known fact that general scattering of the Rayleigh type is more or less polarized when viewed in the direc-

tion normal to the incident radiation. The degree of polarization, however, depends somewhat on the anisotropic character of the molecules. The ratio of the intensity of these horizontal light vibrations (i) to the vertical vibrations (I), gives a measure of the degree of depolarization, that is, $\rho = \frac{i}{I}$ where ρ is the depolarization factor. The vertical vibrations I , are generally preponderant. In the phenomena of diffuse scatterings, that is, scatterings of the Raman spectra type, ρ can reach a value corresponding to $6/7$. The theoretical reasons for this will be given in Chapter 4.

Actual experimental measurements of these polarizations are exceedingly difficult since the experimental arrangement requires the complete elimination of parasitic lights. Cabannes and Rousset employ a source of

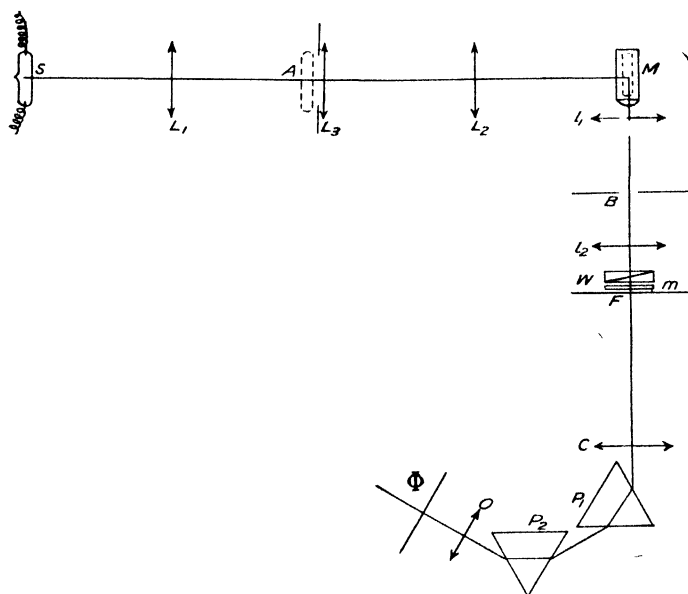


FIGURE 4. A Schematic Diagram of a Method of Determining the Degree of Depolarization of Raman Lines (after Cabannes and Rousset).

incident radiation which is focused on a rectangular slit by means of a lens. The image of the slit is then focused on the Raman tubes. Another lens projects the image of the interior of these tubes onto another rectangular opening and is then reprojected in a similar manner onto the slit of the spectroscope. The Raman radiation diffused at right angles to the incident light consists of two incoherent rectangular vibrations, one of which is of

maximum intensity, I , perpendicular to the incident radiation, and the other is of minimum intensity, i , parallel to the incident radiation. These two beams are resolved by means of a quartz prism placed before the slit, resulting in two spectral images one above the other. A mica plate is used to correct the unequal diminution of i and I in traversing the spectrograph prism. The relative intensity of the two scattered beams may be determined microphotometrically or by other suitable means. This experimental arrangement is shown in Figure 4.

Other observers have used somewhat different experimental arrangements but they are very similar in principle. No brief description, however, can do justice to the care which must be exercised in carrying out the experiment. Bolla^{195, 196} has discussed the rotation of the planes of polarization by the collimating and objective lenses, by the prisms and successive reflections from the photographic plate. The polarization of the edges of Rayleigh lines and the circular polarization of Raman lines have been investigated by Hanle and Heidenreich,⁶⁸⁹ and Reitz¹³⁶³ has discussed the requirements and apparatus for exact polarization measurements. The use of sheets called "Polaroid" to polarize⁵⁴³ or extinguish the incident or diffused radiation will be of value in indicating the relative polarization of Raman lines. This is limited, unfortunately, to radiation between the limits λ 4200-6000. In the course of this presentation polarization data are usually given, when available, together with the magnitude of the Raman shifts, in terms of ρ , the depolarization constant.

Developments in the technique of Raman effect applications have been relatively slow. This is partly because some results are obtainable under almost any circumstances. The importance of further necessary improvements cannot be overestimated. The scope and accuracy of future observations are in a large measure dependent on refinements in procedure already developed and in the continued improvement of the experimental method.

Explanation and Correlation of Terms and Conventions

In presenting the material included in this volume an effort has been made to be as consistent as possible in representing the same quantities by the same abbreviations and names. For diverse reasons this has not always been practicable. Where there has been a departure from the established procedure this has been indicated. There have been times, for example, when a representation of various authors' work according to a uniform system would involve not only the possible introduction of unjustifiable error but also a determination of what is a uniform system. In many cases there is no system, and it is not the purpose of this publication to attempt to establish or to favor any specific system of nomenclature or designation.

Continual usage will possibly result, in time, in its establishment. At present any such attempt would necessarily lead to confusion. It is hoped, however, that by a process of repeated definitions any ambiguity will be avoided.

Apart from definite established usages whose origin is based on publications from different countries, there is also the question of the use of synonyms in English to express the same thing, in order to avoid constant repetition of a particular expression.

First among these are the expressions used to designate what occurs in the Raman effect. The Raman effect involves the appearance of light of certain well defined wave-lengths. From the point of view of definition this is independent of the cause or origin of the effect. The result is that a Raman line may appear on the spectral scale at any place between the x-ray spectrum and the infrared or, in other words, between a fraction of an Ångström unit and 10,000 such units. Its location on this entire scale is dependent on its wave-length. By definition, however, its wave-length may be expressed in various terms. It may be expressed in frequencies or the number of vibrations per second, as frequency is generally defined; or it may be expressed in the number of vibrations per centimeter (wave numbers per centimeter).

In this discussion, the number of vibrations per second is given by $\lambda\nu = 3 \times 10^{18}$, where λ is the wave-length given in Ångström units and the digits represent the velocity of light in the same units—since it has been customary to express wave-lengths of less than 10,000 Ångström units in terms of such units—and ν is the number of vibrations per second. In wave numbers per centimeter this becomes $\lambda\bar{\nu} = 10^8$. ($\bar{\nu} = \nu/c$).

However, the location *per se* of a Raman line in the spectral scale is without significance. As has been pointed out, the important fact is the difference, as measured in Ångström units or, preferably, in the number of vibrations per centimeter, between the exciting radiation and each Raman line. This has been discussed in the first chapter, but to make it doubly clear it should be emphasized again *that the Raman effect is expressed in terms of a difference between two effects: namely, the original source of illumination and the Raman lines, both being expressed in the number of vibrations per second or in wave numbers.*⁹

On this basis the allocation on the spectral scale of the two lines, *i. e.*, the incident radiation and the Raman line, are defined by $\lambda\bar{\nu}_1 = 10^8$ and $\lambda\bar{\nu}_2 = 10^8$, where $\bar{\nu}$ is the number of vibrations per centimeter and λ the wave-length in Ångström units. Therefore, the difference between the exciting radiation and the Raman line is the difference between $\bar{\nu}_1$ and $\bar{\nu}_2$. Such a difference according to accepted mathematical procedure is termed

$\Delta\bar{\nu}$ and represents the difference between the two important factors involved in the Raman effect.

‘Consequently $\Delta\bar{\nu}$ is the wave number difference between the exciting frequency and a given Raman line.’ For rhetorical reasons, and also by common acceptance, this difference is commonly named Raman shift, Raman effect, line, displacement or frequency.’ While the latter terminology may not always be strictly accurate it is one which is very frequently used. In addition to this there will be used the term Raman scattering, as a generic term differentiating the Raman effect from Rayleigh scattering. Occasionally used also are the terms Stokes and anti-Stokes lines. The Stokes lines are identical with Raman lines or Raman shifts. The term anti-Stokes is used exclusively to designate those Raman lines which appear on the spectral scale at a wave-length less, or at a higher frequency than the exciting or incident radiation. ‘These lines occur because they are emitted by molecules in a higher energy level than the normal ones, and their intensities are in proportion to the number of molecules which are in a higher energy state.’ The $\Delta\bar{\nu}$ values, however, of the Raman displacements, frequencies, lines or shifts are the same as the Raman lines which occur ordinarily.

Other expressions are sought to indicate that certain compounds have Raman lines. To avoid constant repetition it may be said that certain substances yield, give rise to, have, exhibit, possess, etc., Raman lines. It may be stated that from, in, for, by, these substances are obtained, recorded, noted, observed, etc., the Raman lines. In all cases these expressions are used synonymously.

In all cases the *magnitudes* of the Raman shifts or Raman lines, etc., means the actual values in wave numbers *between* the incident radiation and the *observed* Raman lines as they appear in the spectrum. It is to be pointed out for the sake of clarity that the statement that the Raman frequency is small means that the wave number shift is small; and this is not to be confused with the fact that, excluding anti-Stokes lines, the *actual frequency* in vibrations per second corresponding to the Raman line on the spectral scale is less with a *large* Raman shift than it would be with a small one. On the other hand as $\Delta\bar{\nu}$ increases this corresponds to an increase in vibrations per second, since $\nu = 3 \times 10^{10} \bar{\nu}$.

Another of the important factors defining the results obtainable from the Raman effect is the intensity. As pointed out in the section on experimental methods, intensities are measured by visual observation or by microphotometric means, and as a whole represent reasonable approximations and not too accurate values. In the course of this presentation it has been attempted to correlate the intensities reported by different observers on the basis of 0 to 10, and, in exceptional cases, an extremely faint line

may be designated as 00. In many of the original publications the actual intensities have been designated as weak, medium, and strong, or by other terminology. It would serve no useful purpose, in view of the uncertainty involved in measuring these intensities, to attempt to set up tables using two or three different means of designating intensities. The consequence of this has been that the writer has repeatedly interpreted and evaluated the intensities designated in French, Italian and German publications in a variety of ways, in terms of a scale from 0 to 10, regardless of the original designation. This may introduce some error, but it is felt that the errors so introduced are less than the misunderstanding that would arise from any attempt to include several systems of intensity designations.

In all the tables given in the text the magnitude of the Raman effect is recorded first. In parentheses follows the intensity, when the amount of the intensity is given.

The third important factor in defining the Raman effect is the degree of depolarization. As has been mentioned this is the ratio of the intensity of the horizontal light vibrations (i) to the vertical vibration (I)—which is generally preponderant—and gives a measure of the degree of depolarization: that is, $\rho = \frac{i}{I}$ where ρ is the depolarization factor or the depolarization constant. In the symmetrical types of vibration this approaches 0 and in the asymmetrical types it may attain a value of 6/7. *In the tables this is the third value which may be given in parentheses when such data are available.* In other words, there are three factors which define the Raman effect: the first is the $\Delta\bar{\nu}$ shift which is given in numerical digits, followed by a value in parentheses which represents the intensity; and this may be followed again by another value, varying from 6/7 to 0, which represents the degree of depolarization. There are other expressions used for the degree of depolarization besides ρ . Frequently, when the value is determined only roughly, it may be designated by D, meaning depolarized, or P, meaning polarized.

Another term used is the value ν which may have various subscripts and represents indirectly a type of vibration which has a definite frequency (ν). For example, the terms ν_π and ν_σ represent the parallel vibrations and the unsymmetrical or asymmetrical types of vibration which may occur in infrared absorption or, in other words, when the change in electric moment is parallel or perpendicular to the symmetry (or figure) axis. There are two other terms which are used in this connection. These are δ_π and δ_σ . These lines refer to the deformation types of oscillation which are parallel or perpendicular to the symmetry axis. In more complicated molecules, or even in simple ones for that matter, these types of vibration may be represented by ν_1 and ν_2 , etc. To indicate roughly the relationship

Table 2. Some General Information About the Common Types of Molecules.

Type of Molecule	Symmetry	Expected number of fundamental vibrational Raman lines present	Notation used to designate Type of Vibration	Polarization (P, polarized; D, depolarized)	Degeneracy (Digits denote degree of degeneracy)	General Relative Magnitude of Raman Shifts (Smallest to greatest)	Examples
AA	$C_{\infty h}$	1	ν_1 sym.	P			H_2
AB	$C_{\infty h}$	1	ν_1 sym.	P			HCl
BAB Linear	$D_{\infty h}$	1	(a) ν_1 (b) ν_r	P			CO_2
AAB or ABC Linear Unsym	C_{2v}	3	ν_1 ν_2 ν_3 ν_{r1} δ_r ν_{r2}	P P D		ν_2, ν_1, ν_3	COS
BAB Non-linear	C_{2v}	3	ν_1 ν_2 ν_3 ν_r δ_r ν_σ	P P D		ν_2, ν_1, ν_3	SO_2
BAB Triangular	C_{3v}	3	ν_1 ν_2 ν_3 ν_r δ_r ν_σ	P P D		ν_2, ν_3, ν_1	NO_2^-
AB ₃ Plane Triangle	D_{3h}	3	ν_1 ν_2 ν_4 ν_r ν_σ δ_σ	P D D	2 2	$\nu_4, (\nu_2), \nu_1, \nu_r$	NO_3^-

AB_3 Pyramidal	C_{3v}	4	$\underbrace{\begin{matrix} \nu_1 & \nu_\pi \\ \nu_2 & \nu_\sigma \\ \nu_3 & \delta_\pi \\ \nu_4 & \delta_\sigma \end{matrix}}_{(a)} \quad \underbrace{\begin{matrix} \nu_1 & \nu_\pi \\ \nu_2 & \delta_\pi \\ \nu_3 & \nu_\sigma \\ \nu_4 & \delta_\sigma \end{matrix}}_{(b)}$	$\begin{matrix} (a) & (b) \\ P & \\ D & P \\ P & D \\ D & \end{matrix}$	$\begin{matrix} (a) & (b) \\ 2 & \\ 2 & 2 \\ 2 & 2 \end{matrix}$	$\begin{matrix} (a) & (b) \\ \nu_4, \nu_3, \nu_2, \nu_1 \\ \nu_4, \nu_2, \nu_3, \nu_1 \end{matrix}$	PCl_3
$ABBA$ Linear	$D_{\infty h}$	3	$\begin{matrix} (a) & (b) \\ \nu_1 & \nu_{0s} \\ \nu_2 & \nu_{1s} \\ \nu_3 & \delta_g \end{matrix}$	$\begin{matrix} P \\ P \\ D \end{matrix}$	2	ν_5, ν_1, ν_2	C_2H_2
AB_4 Tetrahedral	T_d	4	$\begin{matrix} \nu_1 & \nu_\pi \\ \nu_2 & \delta_\pi \\ \nu_3 & \nu_\sigma \\ \nu_4 & \delta_\sigma \end{matrix}$	$\begin{matrix} P \\ D \\ D \\ D \end{matrix}$	$\begin{matrix} 2 \\ 3 \\ 3 \\ 3 \end{matrix}$	$\nu_2, \nu_4, \nu_1, \nu_3$	$SnCl_4$
AB_3C Tetrahedral	C_{3v}	6	$\underbrace{\begin{matrix} \nu_1 & \parallel \\ \nu_2 & \perp \\ \nu_3 & \parallel \\ \nu_4 & \perp \\ \nu_5 & \parallel \\ \nu_6 & \perp \end{matrix}}_{(a)} \quad \underbrace{\begin{matrix} \nu_1 & \parallel \\ \nu_2 & \parallel \\ \nu_3 & \parallel \\ \nu_4 & \perp \\ \nu_5 & \perp \\ \nu_6 & \perp \end{matrix}}_{(b)}$	$\begin{matrix} (a) & (b) \\ P & P \\ D & P \\ P & P \\ D & D \\ P & D \\ D & D \end{matrix}$	$\begin{matrix} (a) & (b) \\ 2 & \\ 2 & 2 \\ 2 & 2 \\ 2 & 2 \end{matrix}$	$\begin{matrix} (a) & (b) \\ \nu_5, \nu_6, (\nu_3 \nu_4) \nu_1 \nu_2 \\ \nu_3, \nu_6 (\nu_2 \nu_5) \nu_1 \nu_4 \end{matrix}$	CH_3Cl
AB_6 Octahedral	O	3	$\begin{matrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{matrix}$	$\begin{matrix} P \\ D \\ D \end{matrix}$	$\begin{matrix} 2 \\ 3 \end{matrix}$	ν_3, ν_2, ν_1	TeF_6

of the mode of vibration to the figure axis or to the center of symmetry, the symbols $\parallel$ for parallel and $\perp$ for perpendicular may be used. The symbols ν_π , ν_σ , δ_π , δ_σ as designations are employed in the German literature, particularly by Mecke and Sponer. Magat and others use slightly different systems.

In this publication the designation of the types of vibration by means of ν with various numerical subscripts will be employed most frequently. The system used by Mecke will be used occasionally. The subscripts to the term ν , such as ν_1 , ν_2 , ν_3 , etc., do *not* designate the same type of vibration for all molecules. The designation is consistent, however, within a given class of molecules, for example, linear molecules of the type AB_2 , pyramidal molecules of the type AB_3 and tetrahedral molecules of the type AB_4 . With pyramidal molecules there are current two systems of designation: first ν_1 , ν_2 for the largest and smallest shifts corresponding to the two parallel vibrations, and ν_3 , ν_4 for the largest and smallest shifts corresponding to the perpendicular vibrations; secondly ν_1 , ν_3 and ν_2 and ν_4 , corresponding to the same types of vibration named above. The latter system is the one adopted for the sake of uniformity, irrespective of the system employed by the original authors. For the purpose of comparison there are shown in Table 2 some of the alternative designations. These are for some of the more common types of molecules. The modes of oscillation which give rise to infrared absorption but no Raman lines, that is, infrared active and Raman inactive, are either not included or given in parentheses. The order given for the magnitude of the shifts as a function of the type of binding is not always constant. This depends, partially, at least, on whether the valence force system or the central force system is applicable. These systems of describing interatomic attraction will be discussed later. For the present it may be mentioned that the pyramidal molecule AB_3 —exemplified in the above table by phosphorus trichloride—may have a different order of frequency types of vibration from those given above for system (a) or (b). For ClO_3 or BrO_3 ions, for example, the order [using notation system (a)] is ν_4 , ν_3 , ν_1 , ν_2 corresponding to the lowest to highest Raman shifts. Then again, in the molecule of the type AB_4 , the respective order for silane (SiH_4) is ν_4 , ν_2 , ν_3 , ν_1 , for methane ν_4 , ν_2 , ν_1 , ν_3 , and for molybdenum tetroxide (MoO_4) ν_2 , ν_4 , ν_3 , ν_1 . These departures from the examples given in the tables represent a rather limited number of compounds and are readily recognized by means of polarization measurements.

In most cases in the text when the type of vibration is discussed, the particular system of nomenclature employed will be described for the sake of clarity even at the expense of excessive repetition. Part of this confusion of terminology is unavoidable; some, however, is due to the fact that no uniform standards have been adopted.

Occasionally it is unavoidably necessary to use the same letter to designate both wholly unrelated qualities and also similar qualities. This is partly because the English language possesses but twenty-six letters (ignoring for the moment Greek letters), and partly because certain letters have by common consent become identified with specific usages. In all cases, however, either the exact meaning is clear from the context or a definition is given *in situ*. Some of these are summarized below, although all will possess various subscripts or superscripts as a special differentiating feature.

- a A proportionality constant usually relating a force to a displacement.
- $\bar{a}$ The greatest amplitude of vibration.
- c The velocity of light.
- c A proportionality constant.
- C Specific heat.
- D The distance between specific atoms.
- D Degree of depolarization, usually referring to inexact measurements but sufficiently accurate to distinguish depolarization from polarization.
- D An amplitude of vibration.
- $\vec{E}$ The electric vector.
- F Usually refers to a force but may occasionally represent the force constant in dynes per centimeter.
- h Planck's constant, 6.54×10^{-27} erg seconds.
- i The intensity of Raman lines on a basis of 0 to 10.
- I The moment of inertia.
- J The rotational quantum number.
- ΔJ Changes in the rotational quantum number.
- K With various subscripts this represents the force constant of an angle.
- $\bar{K}$ With various subscripts this represents the force constant of an angle in a different type of molecule.
- k With different subscripts this is the valence force constant.
- k Boltzmann's constant: 1.37×10^{-16} erg per degree.
- k' With various subscripts this is the force constant in the central force model.
- M The dipole moment or $\vec{M}$ when used as a vector.
- m A mass. This may also be expressed by M .
- N Avogadro's number: 6.06×10^{23} .
- n n th term.
- n The number of normal vibrations. Excluding degeneracy a linear symmetrical molecule has $3n - 5$ and a nonlinear

molecule $3n - 6$ normal vibrations resulting in Raman frequencies.

- P Polarized—as determined approximately.
- R The gas constant, 8.31 ergs per °C per mole.
- r The distance between atoms or the distance a given mass is from the center of gravity of the molecule.
- α May represent the valence angle between two bands.
- α Frequently a constant.
- α May represent the polarizability when it is a tensor, and as α represents a value of a component of such a tensor.
- α^s Represents the spherical polarizability and as α^s stands for any component of this polarizability.
- α^a Represents an isotropic part of the polarizability, and as α^a it is a value of a component of such a tensor
- β Generally a constant.
- δ Usually refers to a deformation type of vibration.
- Δ An increment.
- η One of the axes of a Cartesian coordinate system.
- ζ One of the axes of a Cartesian coordinate system.
- λ Wave-length in Ångström units.
- μ Wave-length in microns.
- $\bar{\mu}$ Reduced mass.
- ν With various subscripts, represents the type of vibration.
- ν Frequency in vibrations per second.
- $\bar{\nu}$ Frequency in wave numbers per centimeter.
- $\Delta\bar{\nu}$ The value in wave numbers per centimeter of the Raman shifts.
- ρ Degree of depolarization measurement, with a fair degree of accuracy. This varies from 0 to 0.75.
- ξ One of the axes of a Cartesian coordinate system.

Of course these examples do not represent all the terms and conventions employed. Variations from these usages are explained, as has been stated previously, whenever necessary. This presentation, however, may be of use as a general guide.

Chapter 3*

The Vibration and Rotation of Polyatomic Molecules

VIBRATION

Since the Raman effect owes its origin to changes of polarizability during intramolecular motions, it is essential to any treatment of this subject to discuss first the nature of these motions or, more specifically, the vibration and rotation of polyatomic molecules.

In a system of more than two atoms held in equilibrium positions by forces acting between them, much more complicated vibrations will result than in diatomic molecules. The reason for this is that while in a diatomic molecule a small displacement will give rise to a force which points straight back to the equilibrium position, in a polyatomic molecule displacements may produce forces which point in a direction different from that in which the displacement takes place.

This condition may be illustrated by a simple model which, though containing only one mass point, shows the main problem of the vibration of polyatomic molecules. Suppose a mass point m to be maintained in an equilibrium position by two pairs of harmonic springs, that is, springs in which the force produced is proportional to the displacement. One spring is placed perpendicular to the other, and both are fastened to a heavy frame as shown in Figure 5. Assume spring S_1 to be weaker than S_2 . If now m is displaced in the direction of S_1 , this spring will push it back to its equilibrium position and a vibration along S_1 will result. Since S_1 is supposed to be weaker than S_2 , this vibration will have a low frequency. Similarly, if m is displaced along S_2 , a faster vibration in the S_2 direction will result. If, however, the direction of displacement is at a 45° angle from S_1 and S_2 the situation will be more complicated. The components of the displacement along S_1 and S_2 will be the same in this case, but, since S_2 is stronger than S_1 , the elastic force along S_2 will be greater than along S_1 . Thus the restoring force will not point in the same direction as the displacement which caused it.

Nevertheless the general vibration of this model can be obtained in a simple way. It must, however, be kept in mind that the component of the

* Chapters 3 through 6 have been written by James H. Hibben and Edward Teller.

force along S_1 depends solely on the displacement along S_1 , and is proportional to this displacement. Similarly the component of the force along S_2 depends solely on the displacement in that direction. Therefore the motions along S_1 and along S_2 will take place independently, and the resulting motion will simply be obtained by saying that both the S_1 and S_2 components vibrate simultaneously, although generally with different amplitudes and different phases. Although such motion may appear to be complicated, it becomes simple if it is regarded through a cylindrical lens which leaves

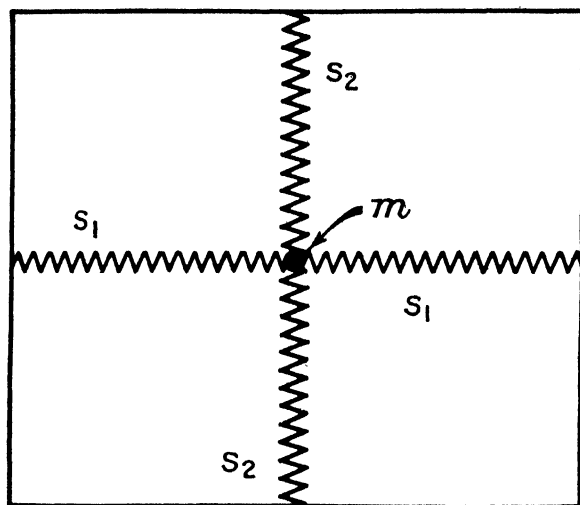


FIGURE 5. A Mass Point m Held in an Equilibrium Position by Two Pairs of Unequal Harmonic Springs, S_1 and S_2 , Placed Perpendicular to Each Other.

the motion along one of the axes (*e.g.*, S_1) unchanged and diminishes the other (S_2) so strongly that it becomes inappreciable.

The vibrations along S_1 and S_2 will be called the normal vibrations of this system. The general motion described above will be called the superposition of the motions along S_1 and S_2 , that is, the superposition of the two normal vibrations.

If the two springs holding m are not perpendicular to each other as shown in Figure 6, the problem seems more complicated but, in reality, the situation will remain essentially unchanged. It can be shown that there will be two directions, indicated by arrows in Figure 6, which are perpendicular to each other and which have the property that a displacement along either of them will produce a force pointing straight back to the origin. Simple vibrations in these two directions will be possible. These will again

be called normal vibrations. It can be shown, moreover, that the most general vibration will consist of a superposition of the two normal vibrations.

Before applying these concepts to polyatomic molecules a few simplifying assumptions will be introduced. In a real molecule, only the relative positions of the atoms are fixed by the equilibrium configuration, and the molecule as a whole (at least in the gaseous state) can perform true translations and rotations. It will prove simpler, however, to discuss the case in which the molecule as a whole is bound to an equilibrium position and an equilibrium orientation with elastic forces, so that each atom of the

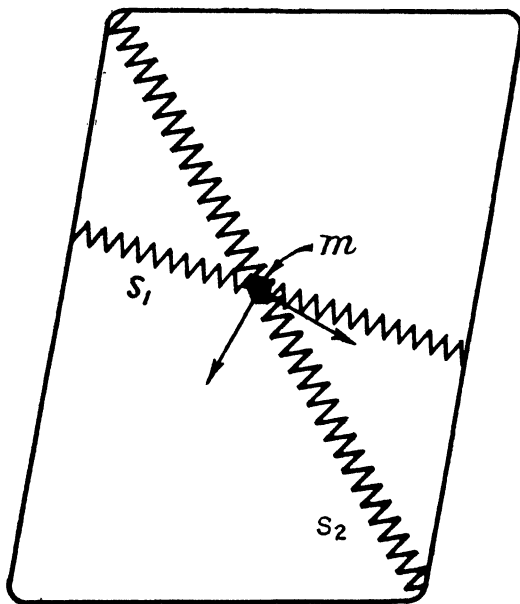


FIGURE 6. A Mass Point Held in an Equilibrium Position by the Springs, S_1 and S_2 , which are not Perpendicular to Each Other.

molecule will have a definite equilibrium position in space. It will be easy later to describe the case of a molecule with free translation and free rotation by letting the forces which restrict the translation and rotation approach zero.

It will be supposed further that the forces acting between the atoms of the molecule are harmonic. This means two things. (1) The forces caused by a displacement from the equilibrium configuration are proportional to the magnitude of the displacement. (2) If there are two displacements and if the first causes a force F_1^i acting on the first atom, F_2^i acting on the second atom, F_i^i acting on the i th atom, while the second displacement

causes the forces $F_1^{\text{II}}, F_2^{\text{II}}, F_4^{\text{II}}$, acting on the same atoms, then the sum of the two displacements will produce the forces $F_1^{\text{I}}+F_1^{\text{II}}, F_2^{\text{I}}+F_2^{\text{II}} \dots, F_4^{\text{I}}+F_4^{\text{II}}$, where $F_1^{\text{I}}+F_1^{\text{II}}$ is the vector sum of the forces F_1^{I} and F_1^{II} . The two statements above can be summarized in mathematical form by saying that the forces are obtained by multiplying the displacements with certain coefficients and adding them, that is, the forces are homogeneous linear functions of the displacements.*

In a real molecule the forces are not strictly harmonic. In fact, in the dependence of the forces on the displacements quadratic (or even higher order) terms may appear. But for small displacements the terms proportional to the first power of the displacements become, of course, more important than terms proportional to the higher powers. In general it will be a reasonable guess, although it might be wrong in special cases, that the ratio of the quadratic terms to the linear terms is of the same order of magnitude as the ratio of the displacement of the atoms to the distance of their nearest neighbors in the molecule.

Normal Vibrations

A normal vibration may now be defined from the above considerations. A normal vibration is one in which all atoms move on straight lines in a harmonic manner (*i.e.*, their elongation from the equilibrium position as a function of time is $a_i \sin \nu t$) and in which all atoms move not only with the same frequency but also in the same phase with possibly different amplitudes (a_i). More crudely it can be said that a normal vibration is one in which all atoms move on straight lines and in phase—although the phase requirement will be somewhat modified in a subsequent definition.

Another, and equivalent, description would be the following: a normal vibration is one in which the forces produced by the displacement in each atom shall be directed toward the equilibrium position of this atom; moreover the force produced in each atom shall be proportional to the displacement of the atom and to its mass. If the atoms in a molecule are subjected to such a displacement, that is, being displaced by varying amounts in varying directions, and are then allowed to oscillate freely, they will execute normal vibrations. This may be seen in the following way. The acceleration of each atom is equal to the force acting on it divided by the mass of the atom. It will be proportional also to the displacement and will be directed toward the equilibrium position. Therefore the atoms will gain velocities in directions opposite to the original displacements, and their velocities will be proportional to the original displacements. After a short time a new displacement will be produced which differs from the original one only in that each displacement vector has been multiplied by the same factor (smaller than unity). The

* Although F occurs as a vector, this is not indicated here, to avoid confusion.

accelerations will still be pointing toward the equilibrium position and will still satisfy the proportionalities described above. A vibration therefore results in which the displacements, accelerations and velocities of the atoms retain the same ratios as were given by the original displacements of the atoms. Thus all atoms move in phase and normal vibrations occur.

The description of normal vibrations just given leads to their quantitative determination. It is only necessary to set up a proportionality between the harmonic forces produced by a displacement on the one hand, and the products of atomic displacements and atomic masses on the other.

The formulas will become simpler if the following convention is introduced: The displacement of the first atom in the x direction will be denoted by ξ_1 , its displacements in the y and z directions by ζ_2 and ζ_3 respectively. The x -, y - and z - displacements of the second atom will be ξ_4 , ξ_5 and ξ_6 ; the displacements of the i th atom, ξ_{3i-2} , ξ_{3i-1} and ξ_{3i} . The coördinates thus introduced are: $\xi_1, \xi_2, \dots, \xi_n$ where $n/3$ is evidently the number of atoms which the molecule possesses, and n is equal to the number of degrees of freedom of the molecule. Similarly, F_1, F_2 and F_3 will denote the x, y and z components of the force acting on the first atom, and F_{3i-2}, F_{3i-1} and F_{3i} , the components acting on the i th atom.

It is now necessary to set up the proportionality between the forces and the products of masses and displacements. This is given by

$$(11) \quad F_1 = -cm_1\xi_1, \quad F_2 = -cm_2\xi_2, \quad \dots, \quad F_n = -cm_n\xi_n.$$

Here c is a proportionality constant which is characteristic for the normal vibration, and the letter m with varying subscripts represents the atomic masses. Thus if $m_1 = m_2 = m_3$ is the mass of the first atom, $m_4 = m_5 = m_6$ of the second, and $m_{3i-2} = m_{3i-1} = m_{3i}$ of the i th, then denoting the second derivative of ξ_i , with regard to the time by $\ddot{\xi}_i$, where $\ddot{\xi}_i$ is the acceleration of the degree of freedom ξ_i , the following equation results:

$$(12) \quad F_1 = m_1\ddot{\xi}_1 = -cm_1\xi_1, \quad F_2 = m_2\ddot{\xi}_2 = -cm_2\xi_2, \dots, \quad F_n = m_n\ddot{\xi}_n = -cm_n\xi_n$$

and therefore

$$(13) \quad \ddot{\xi}_1 = -c\xi_1, \quad \ddot{\xi}_2 = -c\xi_2, \quad \dots, \quad \ddot{\xi}_i = -c\xi_i, \quad \dots, \quad \ddot{\xi}_n = -c\xi_n$$

The differential equations (13) can be satisfied by setting

$$(14) \quad \xi_i = \xi_i^0 \sin 2\pi\nu t$$

where ξ_i^0 is the amplitude and ν the frequency of the vibration. Indeed, if (14) is substituted into (13) it can be seen that the equations (13) are satisfied if

$$(15) \quad 4\pi^2\nu^2 = c$$

It is seen from (14) that all atoms will vibrate with the same frequency, ν , and with the same phases.

In order to find out the values of the amplitudes ζ_i^0 of the vibrations of the various degrees of freedom, the connection between the forces and the displacements which cause them must be described. Since the forces are harmonic they depend only on the first powers of the displacements. Thus,

$$\begin{aligned}
 F_1 &= a_{11}\zeta_1 + a_{12}\zeta_2 + \dots + a_{1n}\zeta_n \\
 F_2 &= a_{21}\zeta_1 + a_{22}\zeta_2 + \dots + a_{2n}\zeta_n \\
 &\vdots \qquad \qquad \qquad \vdots \qquad \qquad \qquad \vdots \\
 F_n &= a_{n1}\zeta_1 + a_{n2}\zeta_2 + \dots + a_{nn}\zeta_n
 \end{aligned}
 \tag{16}$$

where a_{11} , a_{12} and a_{1n} [or a_{ik}] stand for constant coefficients which are characteristic for the molecule under consideration. These are called the force constants. The interpretation of equation (16) is that, in general, any displacement ζ_k , which is the displacement of a certain atom in the x , y or z direction as the case may be, shall produce a force F_i of the magnitude $F_i = a_{ik}\zeta_k$ which may possibly act on another atom in another direction. This is the most general assumption which can be made about harmonic forces and, considering the complicated way in which the atoms of a molecule may interact, such an assumption is necessary. The ultimate purpose of many investigations of molecular vibrations (with the help of the Raman effect, infrared spectra or specific heats) is to find out the force constants a_{ik} and thereby obtain detailed information about intramolecular forces.

Substituting (11) in (16) there is obtained

$$\begin{aligned}
 -cm_1\zeta_1 &= a_{11}\zeta_1 + a_{12}\zeta_2 + \dots + a_{1n}\zeta_n \\
 -cm_2\zeta_2 &= a_{21}\zeta_1 + a_{22}\zeta_2 + \dots + a_{2n}\zeta_n \\
 &\vdots \qquad \qquad \qquad \vdots \qquad \qquad \qquad \vdots \\
 -cm_n\zeta_n &= a_{n1}\zeta_1 + a_{n2}\zeta_2 + \dots + a_{nn}\zeta_n
 \end{aligned}
 \tag{17}$$

Equations (17) hold for the displacements ζ_i at any moment of the vibration and therefore also for the moment of maximum elongation when the ζ_i 's have the values ζ_i^0

$$\begin{aligned}
 -cm_1\zeta_1^0 &= a_{11}\zeta_1^0 + a_{12}\zeta_2^0 + \dots + a_{1n}\zeta_n^0 \\
 -cm_2\zeta_2^0 &= a_{21}\zeta_1^0 + a_{22}\zeta_2^0 + \dots + a_{2n}\zeta_n^0 \\
 &\vdots \qquad \qquad \qquad \vdots \qquad \qquad \qquad \vdots \\
 -cm_n\zeta_n^0 &= a_{n1}\zeta_1^0 + a_{n2}\zeta_2^0 + \dots + a_{nn}\zeta_n^0
 \end{aligned}
 \tag{18}$$

Equation (18) could have been obtained from (17) also by substituting (14) and dividing by $\sin 2\pi\nu t$.

Equations (18) may be used to determine the amplitudes ξ_i^0 with which the ξ_i 's vibrate in a normal vibration. There is, of course, a simple solution if all the ξ_i 's are equal to zero. Then equation (18) is satisfied but leads to an uninteresting solution since it only means that no vibration takes place.

Furthermore, if a set of ξ_i^0 values (not all equal to zero) which satisfy (18) has been found, then one may multiply all the ξ_i^0 's with one and the same number and get a new set of ξ_i^0 's which again satisfy the equation, because multiplication of all ξ_i^0 's with the same number merely means a multiplication of both sides of (18) by this number. This statement means that if a normal vibration has been found, all its amplitudes may be multiplied by the same number and there will still remain a normal vibration. It may be stated, therefore, that the absolute values of the amplitudes are not characteristic for the normal vibration but only the relative amplitudes of vibration of the different degrees of freedom. The ratio of these amplitudes with which the several atoms vibrate in the x , y and z directions constitutes what may be called the *form of vibration*.

In general, however, no solution will be found except the uninteresting one in which all ξ_i^0 values are zero. The theory of systems of homogeneous linear equations demonstrates that a solution is possible only for specialized values of the constant c appearing in equation (18). In particular a solution will be found if the determinant of equation (18) vanishes, *i. e.*, if

$$(19) \quad \begin{vmatrix} a_{11} + m_1 c & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} + m_2 c & \dots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} + m_n c \end{vmatrix} = 0$$

Equation (19) can be regarded as an equation of the n th degree which has to be solved for the unknown constant c . It can be satisfied, therefore, either for n or for less than n different values of c .

It can be shown that if all atoms of the molecule have a stable equilibrium position, all solutions of c will be positive. From equation (15) can be found the frequency, ν , which belongs to a particular solution of c .

The simplest case in which the n th degree equation (19) has n different solutions will be considered first. In this case for each c value which satisfies (19) the system of equations (18) can be solved in one definite way characterized by the *ratio* of the values ξ_i . Thus in this simplest case the molecule has n different "forms of vibration." Therefore *the number of*

different normal vibrations is equal to the number of degrees of freedom of the molecule.

Degenerate Vibrations

It may happen, however, that (19) has less than n different solutions. In this case a new phenomenon called degeneracy appears. Degeneracy means that two or more different forms of vibration, and therefore two or more normal vibrations, belong to the same frequency. The vibration is then called a degenerate vibration. Before discussing this in general terms there will be mentioned a special example which can be understood from the model mentioned in the beginning of this chapter and illustrated in Figure 5.

If in Figure 5 the two springs S_1 and S_2 are assumed to have equal strength, then the vibration along S_1 and S_2 will proceed with the same frequency. Thus the ν values and, according to (15) also the c values, will be the same for the two normal vibrations, thus leading to an example of degeneracy.

An important property of degenerate vibrations can be studied with the help of this example. Consider first a displacement in a direction at an angle of 45° from S_1 and S_2 . Then the components of the displacements along S_1 and S_2 will be equal and, as S_1 and S_2 have now the same strength, the components of the elastic force along S_1 and S_2 are also the same. A force will result, therefore, which points straight back to the equilibrium position. Moreover it can easily be seen that this force will be just as great as the one which is caused by a displacement of the same magnitude in the S_1 or S_2 direction. It follows that a normal vibration may now also be obtained at 45° to S_1 and S_2 and that this normal vibration has the same frequency as those along S_1 and S_2 . It is readily apparent that this holds for any other direction and that a normal vibration of the same frequency is possible along any straight line passing through the equilibrium position.

This can be demonstrated from another point of view. It has been stated that the most general motion of the point m may be obtained by superposition of the vibrations along S_1 and S_2 . Since, in the present case, the vibrations along S_1 and S_2 have the same frequency, one may superpose two vibrations along S_1 and S_2 which remain constantly in the same phase. The result will be a vibration along a straight line lying between S_1 and S_2 . The angle will be determined by the ratio of the original amplitudes along S_1 and S_2 .

If now two vibrations (along S_1 and S_2) which have the same frequency but differ in their phase are superposed, then a motion along an ellipse will result; or this may be a circle if the phase difference is a quarter

of a vibration period. This elliptical motion is usually also called a normal vibration although it does not conform to the original definition previously given. The general definition of a normal vibration must therefore be modified in the following way: A normal vibration is a vibration in which all degrees of freedom vibrate with the same frequency. It is not required that they should vibrate with the same phase. For non-degenerate vibrations, however, the phases also happen to be the same and so the original definition holds in this case.

Although an infinite variety of normal vibrations has been found in the model with the two equal springs, they can all be obtained from only two vibrations by superposing them with varying amplitudes and phases. It is said, therefore, that in this model there is a *twofold degeneracy*.

In the general case statements can be made about degenerate vibrations similar to those that have just been made about the simple model. If there are two different vibrations belonging to the same frequency and, therefore, to the same constant c , any superposition of the two normal vibrations will again be a normal vibration. Thus if

$$\xi_1^I, \quad \xi_2^I \dots \xi_n^I$$

are amplitudes satisfying equations (18) for a certain value of c , and

$$\xi_1^{II}, \quad \xi_2^{II} \dots \xi_n^{II}$$

are another set of amplitudes satisfying (18) for the same value of c , it is easy to verify that the amplitudes

$$\alpha \xi_1^I + \beta \xi_1^{II}, \quad \alpha \xi_2^I + \beta \xi_2^{II}, \quad \dots \dots \alpha \xi_n^I + \beta \xi_n^{II}$$

will also satisfy (18) if α and β are any two constants. Therefore superposition of the two original vibrations with the arbitrary coefficients α and β will again lead to a normal vibration, as has been stated above. This means that if two different normal vibrations belong to the same value of c , an infinity of normal vibrations can be constructed, all belonging to this c value. If, however, all these normal vibrations can be obtained from *two* vibrations with the help of superposition, then there is a *twofold degenerate vibration*.

It may happen also that all vibrations belonging to a certain frequency cannot be obtained by superposition of two different vibrations, but only by superposition of three or more vibrations. In this case this is called a *three- (or more) fold degeneracy*. The two- and threefold degeneracy have the greatest practical significance. A threefold degenerate vibration may be exemplified in a simple way by considering a mass point m held in its equilibrium position by three pairs of springs S_1 , S_2 and S_3 of equal strength and situated at right angles to each other (*e.g.*, pointing in the x , y and z directions respectively).

It is now possible to resume the discussion of the case in which equation (19) has less than n different solutions and in which, therefore, there are less than n different frequencies, ν , for which a normal vibration exists. In this instance it can also be said, in a certain sense, that the molecule has n different normal vibrations, *i.e.*, the number of normal vibrations is again equal to the number of degrees of freedom. To do this one must count each degenerate vibration as two, three or more vibrations according to whether it is two-, three-, or more fold degenerate. Each non-degenerate vibration is of course to be counted as one vibration. It then follows from the theory of linear equations, as applied to the system (18), that there will be just n normal vibrations.

The most general motion of the polyatomic molecule can be obtained by superposing all the normal vibrations with varying amplitudes and phases. Indeed the various normal vibrations can be executed simultaneously without disturbing one another.

In order to consider the molecule in the gaseous state in which it can perform translations and rotations freely, the forces which bind the molecule to an equilibrium position and an equilibrium orientation must be made to approach zero. In this case there will be obtained some particularly slow "normal vibrations" of the molecule, corresponding to the vibration of the molecule as a whole in a certain direction and to a torsional vibration around a certain axis. The frequencies of these slow vibrations will approach zero as the forces which bind the molecule to a certain position and orientation decrease. The vibrations of the molecule as a whole will then go over into the translational motion. The translations may be regarded, therefore, as degenerate vibrations belonging to the frequency zero, the degeneracy being threefold since there are three independent translations (along the x , y , and z directions) out of which the translations in every other direction can be composed. On the other hand the torsional vibrations go over into the rotations of the molecule. For a molecule in which the equilibrium positions of all the atoms are lying in a straight line, there are two independent rotations (around two axes perpendicular to the molecular axis and to each other), and the rotations correspond to a twofold degenerate vibration with the frequency zero. If all the atoms do not lie on a straight line there are three independent rotations around three orthogonal axes. These rotations correspond to a threefold degenerate vibration. Thus there will remain $n-5$ and $n-6$ real normal vibrations of a molecule according to whether or not all the atoms lie on a straight line. These normal vibrations differ from translational and rotational vibrations which are, properly speaking, not vibrations at all.

Orthogonality

It is helpful, both in finding the normal vibrations in a special example and also in visualizing them in a qualitative way, to discuss an important property of these vibrations, namely, their *orthogonality*. Orthogonality means that the calculated total work done *by* the forces resulting from the displacement of one normal vibration *on* the displacement of a second normal vibration with a different frequency is zero. This, of course, is closely connected with the fact that normal vibrations taking place simultaneously do not disturb one another.

First this statement is put down in mathematical form. Let

$$\xi_1^I, \quad \xi_2^I, \quad \dots \xi_i^I, \quad \dots \xi_n^I$$

be the displacements of the first normal vibration. The c value for this vibration shall be called c^I . Then the forces acting on the several degrees of freedom will be according to equation (11)

$$-c^I m_1 \xi_1^I, \quad -c^I m_2 \xi_2^I, \quad \dots -c^I m_i \xi_i^I, \quad \dots -c^I m_n \xi_n^I$$

The displacements in the second normal vibration shall be

$$\xi_1^{II}, \quad \xi_2^{II}, \quad \dots \xi_i^{II}, \quad \dots \xi_n^{II}$$

The work which the force $-c^I m_i \xi_i^I$ acting on the i th degree of freedom performs on the displacement ξ_i^{II} will be $-c^I m_i \xi_i^I \xi_i^{II}$. The total work is therefore

$$- [c^I m_1 \xi_1^I \xi_1^{II} + c^I m_2 \xi_2^I \xi_2^{II} + \dots c^I m_n \xi_n^I \xi_n^{II}] = - \sum_i c^I m_i \xi_i^I \xi_i^{II}.$$

Orthogonality of the two vibrations means that this last expression vanishes. Dividing* by $-c^I$ there can be obtained

$$(20) \quad \sum_i m_i \xi_i^I \xi_i^{II} = 0,$$

where equation (20) is the mathematical formulation of the orthogonality of two vibrations. It will be noticed that although in the original definition the two vibrations entered in different ways, in equation (20) they enter in a symmetrical manner.

In order to prove this equation, a property of the force constants must first be shown. The force constant a_{ik} which gives the force acting along the i th degree of freedom and produced by a unit displacement of the k th degree of freedom is equal to a_{ki} which is the force along the k th direction produced by a unit force along the i th direction. This can be shown

* It must be borne in mind that c^I can always be assumed to be different from zero since the orthogonality holds, in general, only if the frequencies—and therefore the c values—differ for the two vibrations. Consequently one may always choose the "first vibration" in such a way that its c value is different from zero.

with the help of the law of the conservation of energy. First a molecule is considered in its equilibrium position in which all the ξ values are zero. If ξ_k is allowed to increase from 0 to 1, then according to (16), the force F_k acting along this direction will be $a_{kk}\xi_k$ and during the displacement the work

$$\int_0^1 a_{kk}\xi_k d\xi_k = 1/2 a_{kk}$$

will be done. Then ξ_i is permitted to increase from 0 to 1. The force F_i however will now be not simply $a_{ii}\xi_i$ but rather

$$a_{ii}\xi_i + a_{ik}\xi_k = a_{ii}\xi_i + a_{ik}$$

since ξ_k has already previously attained the value 1. The work during this second displacement will be, therefore

$$\int_0^1 (a_{ii}\xi_i + a_{ik})d\xi_i = 1/2 a_{ii} + a_{ik}$$

The total work, $1/2(a_{ii} + a_{kk}) + a_{ik}$, is the potential energy of the final configuration in which ξ_i and ξ_k are 1 and all the other ξ 's are zero. If, now, one again begins with the molecule in its equilibrium position and lets first ξ_i , and after it ξ_k , increase from 0 to 1, the same expression will be obtained for the work done, except that the indices i and k will now change their role and there is obtained

$$1/2(a_{ii} + a_{kk}) + a_{ki}$$

This expression must be equal, however, to the potential energy of the same configuration ($\xi_i = \xi_k = 1$, all other ξ 's being zero) which is possible only if

$$(21) \quad a_{ik} = a_{ki}$$

This is the relationship which it was desired to demonstrate.

With the help of (21) the orthogonality (20) can be easily proved. According to (17) equations (22) and (23) hold for the displacements of the two vibrations

$$(22) \quad \begin{array}{l} -c^I m_i \xi_i^I = a_{11}\xi_1^I + a_{12}\xi_2^I + \dots + a_{1n}\xi_n^I \\ -c^I m_2 \xi_2^I = a_{21}\xi_1^I + a_{22}\xi_2^I + \dots + a_{2n}\xi_n^I \\ \vdots \quad \quad \quad \vdots \quad \quad \quad \vdots \quad \quad \quad \vdots \\ -c^I m_n \xi_n^I = a_{n1}\xi_1^I + a_{n2}\xi_2^I + \dots + a_{nn}\xi_n^I \end{array} \left| \begin{array}{l} \xi_1^{II} \\ \xi_2^{II} \\ \vdots \\ \xi_n^{II} \end{array} \right.$$

$$(23) \quad \begin{array}{l} -c^{II}m_1\xi_1^{II} = a_{11}\xi_1^{II} + a_{12}\xi_2^{II} + \dots + a_{1n}\xi_n^{II} \\ -c^{II}m_2\xi_2^{II} = a_{21}\xi_1^{II} + a_{22}\xi_2^{II} + \dots + a_{2n}\xi_n^{II} \\ \vdots \\ -c^{II}m_n\xi_n^{II} = a_{n1}\xi_1^{II} + a_{n2}\xi_2^{II} + \dots + a_{nn}\xi_n^{II} \end{array} \left| \begin{array}{l} -\xi_1^I \\ -\xi_2^I \\ \vdots \\ -\xi_n^I \end{array} \right.$$

Multiplying the i th row of (22) with ξ_i^{II} and the i th row of (23) with $-\xi_i^I$ (the quantity with which each row is multiplied is indicated on the right side of each row) and then taking the sum of all equations (22) and (23), there is obtained

$$(24) \quad -(c^I - c^{II})\sum_i m_i \xi_i^I \xi_i^{II} = \sum_{ik} (a_{ik} - a_{ki}) \xi_k^I \xi_i^{II}$$

The right-hand side of equation (24) vanishes because of equation (21). Since it has been assumed that the two vibrations possess different frequencies and therefore different c values, equation (24) may be divided by $(c^I - c^{II})$ and there is obtained

$$(20) \quad \sum_i m_i \xi_i^I \xi_i^{II} = 0$$

which is the orthogonality relation.

There will be ample opportunity to apply the orthogonality relation when special examples are discussed. One example will be described at once, however, since it helps to visualize the physical significance of the orthogonality relation.

Since, as has been seen above, the translation can be considered as a vibration of the molecule with vanishing frequency, the orthogonality relation may be applied to a translation, *e. g.*, the translation in the x direction on the one hand and to a real vibration on the other. During a translation in the x direction, the x coördinates of all the atoms change by the same amount; we may consider a translation for which all x 's change by 1. The y and z coördinates remain unchanged. If $\xi_1^I, \xi_2^I, \dots, \xi_n^I$ corresponds to the translation, then the ξ_i^I 's will be zero according to whether the particular ξ_i^I is a displacement in the x direction or not. The equation $\sum_i m_i \xi_i^I \xi_i^{II} = 0$ is reduced therefore to the simpler expression $\sum_i m_i \xi_i^{II} = 0$, where in the second equation the summation over i is to be extended only over the displacements in the x direction. The expression $\sum_i m_i \xi_i^{II}$ has a simple significance. It is the distance through which the center of gravity of the molecule is displaced in the x direction, if the displacement ξ^{II} takes place, multiplied by the mass of the molecule. The application of the orthogonality leads therefore to the statement that a normal vibration will not change the position of the center of gravity

ROTATION

Diatomic Molecules

The rotation of a diatomic molecule takes place around an axis perpendicular to the line joining the atoms. A rotation around the molecular axis does not cause any relative motion of the atoms. Although the electrons as well as the atomic nuclei move during rotation, the influence of electronic motion on rotation can generally be disregarded. The frequency of rotation is different for each molecule even at the same temperature and it will increase with an increase in temperature.

Linear Polyatomic Molecules

If the equilibrium positions of all the atoms in the molecule lie on a straight line, then the rotation of the polyatomic molecule will take place in the same way as that of a diatomic molecule. In fact the two rotations will follow exactly the same laws (*i. e.*, the connection between the energy and the frequency of the rotation will be the same) if the *moment of inertia* for the diatomic and polyatomic molecule is the same. The moment of inertia is given by the expression $\sum_l m_l r_l^2$, where m_l is the mass of the l th atom and r_l is its distance from the center of gravity of the molecule. The average rotational energy will increase proportionally to the temperature. The rotational frequencies, which will follow a distribution somewhat similar to the distribution of molecular velocities in a gas, will increase, on the average, with the square root of the temperature. The way these statements have to be modified by the quantum theory will be mentioned later.

Spherical-top Molecules

If all the atoms in a molecule do not lie on a straight line it becomes necessary to speak about moments of inertia around different rotational axes passing through the center of gravity. These moments are given by the expression $\sum_l m_l \rho_l^2$, where ρ is the distance of the l th atom from the axis in question.

A particularly simple case occurs if the moment of inertia around every axis which passes through the center of gravity has the same value. Molecules meeting this requirement are known as spherical-top molecules. Methane, CH_4 , in which the hydrogen atoms lie at the corners and the carbon atom in the center of a regular tetrahedron, is an example.

Spherical-top molecules may perform a simple rotation around any one of these axes, the connection between energy and frequency of vibration being just the same as it would be for a diatomic molecule with the same moment of inertia.

Symmetrical-top Molecules

There are other molecules for which all moments of inertia around axes lying in a certain plane and passing through the center of gravity are the same. The moment of inertia around an axis perpendicular to this plane is, however, different. Such molecules are called symmetrical-top molecules. The axis perpendicular to the plane mentioned above is called the figure-axis of the molecule. Chloroform, CHCl_3 is an example. In this molecule the $\text{H}-\text{C}$ axis is the figure axis.

The rotation of such a molecule is somewhat more complicated. In general the figure axis will execute a uniform precession around an axis fixed in space. The angle between these two axes remains unchanged during the precession and, at the same time, the molecule will rotate around the figure axis.

Asymmetrical-top Molecules

If neither of the above requirements is fulfilled, an asymmetrical-top molecule results. Water is one of the numerous examples. The discussion of its rotation is a complicated mathematical problem and no simple description of its rotation is possible.

Specific Heat

There will be discussed now a manifestation of intramolecular motions, *i.e.*, specific heat, which in turn can be used to secure information about these motions and about molecular structure.

According to classic statistical mechanics, each translational and rotational degree of freedom of a gaseous molecule contributes $R/2$ to the specific heat of the gas, whereas each harmonic vibration adds the amount R . Two-, three-, or more fold degenerate vibrations contribute as much as two, three or more different vibrations would contribute. Thus a diatomic molecule, with 3 translations, 2 rotations and 1 vibration should have the specific heat $C_v = 7/2 R$; a linear triatomic molecule such as carbon dioxide with 3 translations, 2 rotations and $3 \times 3 - 5 = 4$ vibrations, should have $13/2 R$, whereas a non-linear triatomic molecule (H_2O) with 3 translations, 3 rotations and 3 vibrations should have $6R$.

Most gases have, however, smaller specific heats, C_v , than those given above. Moreover the specific heats, instead of remaining constant, increase with temperature. These two facts can be explained with the help of the quantum theory.

According to the quantum theory a vibrational degree of freedom (*i.e.*, the vibration of a diatomic molecule or, in general, a normal vibration of a molecule) can change its energy only by multiples of the energy $h\nu$, where ν is the frequency of the vibration. The number of molecules possessing

one or more such energy quanta is regulated by Boltzmann's law, the relative number of molecules with 0, 1, 2, ... quanta being

$$1, \quad e^{-\frac{h\nu}{kT}}, \quad e^{-\frac{2h\nu}{kT}}, \quad \dots$$

At a low temperature where ($kT \ll h\nu$) both the number of molecules with one or more quanta and also the change of this number with temperature will become vanishingly small, and at low temperatures the vibrations do not contribute to the specific heat. With increasing temperature, however, their contribution increases, until finally at high temperatures ($kT \gg h\nu$) their contribution reaches the classic value R . Starting from the Boltzmann law given above, a simple formula can be derived for the specific heat C_v of a vibration with the frequency ν thus,

$$(25) \quad C_v = R \left(\frac{X}{\sinh x} \right)^2$$

In this formula there is introduced the abbreviation $X = \frac{h\nu}{2kT}$ and $\sinh x$ is the hyperbolic sine of x , that is,

$$(26) \quad \sinh x = \frac{e^x - e^{-x}}{2}$$

The total vibrational specific heat of a molecule with several normal vibrations is obtained if one calculates the contribution of each normal vibration from (25) and then adds the results. Two-, three- or more fold degenerate vibrations should be regarded as two, three or more distinct vibrations with the same frequency.

For a diatomic molecule one reliable measurement of the specific heat at a suitable temperature should be sufficient to calculate the frequency of the vibration. The contributions of the translation, which can be calculated, in general, according to the classic theory, are subtracted from the measured value. For a polyatomic molecule the procedure is more complicated because there still remains the question of how this contribution should be divided among the normal vibrations even after the total contribution of all vibrations is determined. It is possible, however, at least in principle, to obtain all vibrational frequencies by measuring the specific heat as a function of temperature and then decomposing the total vibrational contribution into a sum of functions of the form given in equation (25).

In practice, accurate measurement of the specific heat of gases is so difficult that even for diatomic molecules it is not usual to determine ν from the specific heat. The specific heat method is, however, useful in checking the ν values obtained from other methods, such as infrared spectra and the Raman effect, both for diatomic and for polyatomic molecules. Moreover some frequencies, as will be seen later, cannot be obtained in a direct way

from infrared absorption or Raman spectra. Specific heat measurements are of the greatest importance in obtaining information about these frequencies.

The translational and rotational motions of the molecules usually contribute $R/2$ to the specific heat per degree of freedom, that is, the predictions of classic statistical mechanics concerning translation and rotation are proved to be correct. In fact it can be shown by a quantum mechanical treatment that the translational motion must behave in all practical cases according to classic mechanics. The rotations are, on the other hand, quantized in a simple way; namely, only those rotational frequencies, ν_r , are allowable for which $2\pi\nu_r I = h$, where I is the moment of inertia. This prediction is correct in this simple form only for linear molecules and spherical-top molecules which possess just *one* moment of inertia. Inasmuch as the frequency ν_r and the possible changes in rotational energy are interrelated, this means that only certain rotational energies are permitted, a situation similar to the one encountered in the case of the vibrations. Nevertheless in almost all practical cases kT is much greater than the energy difference between two consecutive rotational states; hence, just as observed for the vibrations at sufficiently high temperature, the classic specific heat is obtained. The only important exceptions are hydrogen, hydrogen deuteride, and deuterium, for which the rotational specific heats at room temperature are still noticeably different from $2\left(\frac{R}{2}\right) = R$.

Chapter 4

General Theory of Infrared Absorption Spectra and the Raman Effect

INFRARED SPECTRA

The vibrations and rotations of polyatomic molecules have been described thus far. Both infrared absorption and the Raman effect are a consequence of these intramolecular oscillations and rotations, and both are so interrelated that it would be inadvisable to proceed with a discussion of the Raman effect itself without first pausing to consider the correlation of infrared absorption with intramolecular motion. It is for this purpose that this subject is introduced here.

Infrared Rotational Spectra

If a molecule possesses a dipole moment, an external electric force will tend to orient it. Thus if light, that is, electromagnetic oscillation, falls on the molecule it will receive periodic impulses tending to orient it first one way and then the other. If the frequency of these impulses coincides with the rotational-frequency of the molecule, the molecule may gain energy while the radiation loses some. In this case absorption will take place. Conversely, if a dipole molecule rotates it will create periodically alternating electric fields, and it will therefore emit radiation while losing the corresponding amount of energy.

According to classic mechanics a diatomic molecule may rotate with any frequency. The number of molecules rotating with a certain frequency depends on the temperature and the moment of inertia. Thus a continuous spectrum of frequencies should be absorbed and emitted. From the intensity distribution in the spectrum, which is determined by the number of molecules having the proper rotational frequency, one may calculate the moment of inertia.

According to the quantum theory, however, not all rotational frequencies ν_r of a diatomic molecule will occur, but only those which satisfy the relation

$$(27) \qquad 2\pi\nu_r I = h$$

(I = moment of inertia and h = Planck's constant). Actually it is found that the rotational spectra of diatomic molecules consist of equidistant lines

rather than a continuum. However, on observing these lines with an instrument of low resolving power, the apparent continuum usually has about the same intensity distribution as predicted by the classic theory. The determination of the moment of inertia I can be carried out with greater accuracy by observing the spacing of the rotational lines than by measuring the intensity distribution. Spectroscopic determination of moments of inertia, when applicable, is one of the most reliable methods of finding the distances between atoms in a molecule.

The statements made about diatomic molecules hold also for linear polyatomic molecules.

Spherical-top molecules have not, as a general rule, dipole moments. They do not interact, therefore, with electromagnetic radiation and do not have any rotational emission and absorption spectra.

The dipoles of symmetrical-top molecules usually lie in the figure axes of the molecules. The rotation around the figure axis does not therefore influence the orientation of the dipole moment. Thus only the frequencies with which the figure axis is precessing can be observed in the rotation spectra; and it is from these frequencies that the moment of inertia around an axis perpendicular to the figure axis can be determined.

The complicated motion of an asymmetrical-top molecule produces many seemingly irregular absorption and emission frequencies. With particularly careful analysis it is possible, however, in a few cases (*c.g.*, water), to deduce the moments of inertia from this complicated spectrum.

Infrared Vibrational Spectra

If the dipole moment changes during a molecular vibration, a periodically changing electric field will be produced around the molecule, and emission and absorption of the vibration frequency will occur. Ordinarily, diatomic molecules consisting of two similar atoms, such as hydrogen or nitrogen, would not emit and absorb their vibrational frequency because such molecules would retain an electrical moment equal to zero during their vibration. It is possible, however, that a molecule which, in its equilibrium position, does not possess a dipole moment would emit and absorb vibrational frequencies, since the displacement during the vibration may produce a dipole moment; and it is this *change* in dipole moment that gives rise to infrared absorption and emission. Thus carbon dioxide, which has no dipole moment, absorbs and emits two vibrational frequencies, corresponding to asymmetrical vibrations, thus producing dipole moments. This as well as other examples will be discussed later.

If the vibration of a diatomic molecule is purely harmonic, and if the dipole moment is a strictly linear function of the displacement from the equilibrium position, then the electric oscillation will proceed as a simple

sine function of the time, and the actual vibrational frequency of the molecule will be the only one which appears in the vibrational absorption and emission spectra. If, however, the vibration is anharmonic, that is, not strictly harmonic, or if the dipole moment is not strictly a linear function of the displacement, the electric distribution within the molecule will be a more complicated function of time. In this case, apart from the vibrational frequency of the molecule, or the fundamental frequency, other frequencies may appear which are simple whole-number multiples of the fundamental. These correspond to the first, second and higher overtones. The two causes which may give rise to overtones, namely, the anharmonicity of the vibration itself and the non-linear change of the dipole moment with the atomic displacement, are called the mechanical and the electrical anharmonicity.

As a general rule, the electrical forces appearing in light which has been emitted with the fundamental frequency will compare with the electric forces in the first overtone in the same way that the interatomic distance compares with the vibrational displacement of the atoms, *i.e.*, approximately 10:1 or 30:1. The ratio of the intensities of the fundamental and the first overtone is given by the square of the ratio of the electric forces. Thus, as a general rule, the first overtone will be from about a hundred to a thousand times weaker than the fundamental. The second overtone will, in general, be again a hundred to a thousand times weaker than the first overtone; the third a hundred to a thousand times weaker than the second, and so on. This holds both for emission and absorption, but it is a rule which is only crudely approximate. It may even happen occasionally that the fundamental is weaker than the first overtone.

If the vibrations of a polyatomic molecule are strictly harmonic and if the dipole moment depends in a strictly linear manner on the atomic displacements, then not only the normal vibrations but also the changes of dipole moment produced by the normal vibrations will be independent of each other. The result is that the frequencies of the normal vibrations will appear in the vibrational spectrum if the dipole moment of the molecule changes during the normal vibration in question. This change of dipole moment can be determined for each normal vibration separately without regard to the other normal vibrations.

Mechanical or electrical anharmonicity may give rise to overtones in polyatomic molecules. The qualitative rules about intensities of overtones obtained from diatomic molecules apply also to polyatomic molecules. However, there may appear, in addition, sums and differences of fundamentals or overtones which are called combination tones. They occur because the change in the electric moment caused by a normal vibration, and the forces acting during this normal vibration, will be influenced by the displacement

belonging to another normal vibration if the electric moment and the forces are not strictly linear functions of the displacements. Much the same statements can be made about the intensities of combination tones as about the overtones. It may happen, however, that the combination tones of two frequencies may appear, although the fundamentals of these frequencies have a zero intensity.

The slight modifications which have to be introduced on account of the quantum theory will be discussed later.

Infrared Vibrational-Rotational Spectra

The rotation of a diatomic molecule not only affects the direction of the dipole moment but also the direction of the change of dipole moment which takes place during a vibration. The result is that, instead of the vibration frequency ν_v , the sum and difference of vibration and rotation frequency $\nu_v + \nu_r$ and $\nu_v - \nu_r$ will be observed. Since ν_r is always much smaller than ν_v , this means an unimportant change in the vibration frequency. The molecules of the gas rotating with different frequencies, ν_r , will together give rise to a broadened vibration frequency. Thus all frequencies in the neighborhood of ν_v will be present except the frequency ν_v itself, since the probability for $\nu_r = 0$ vanishes in an analogous way as the probability of the zero velocity in the Maxwell velocity distribution. The appearance of the vibrational-rotational spectrum is therefore that of a double band, called the Bjerrum double band. Owing to the quantization of rotation, this double band breaks up into a series of rotational lines. It is frequently more convenient to determine the moment of inertia from the vibrational-rotational spectrum than from the pure rotation spectrum since the latter lies in the far infrared in which measurements are difficult.

When investigating the vibrational-rotational bands through an instrument of poor resolution, one finds a continuous double band with an intensity distribution approaching closely that predicted by the classic theory. If the resolution becomes still poorer, this double band is apparently reduced to a single line which has just the same appearance as if the molecules were not rotating at all but were distributed with random orientation in space. The poor resolution means only that the apparatus is not sensitive enough to reveal the relatively small rotational frequency, in consequence of which the molecules do not appear to rotate.

If in a linear polyatomic molecule the vibration will cause a change of dipole moment along the molecular axis, the corresponding vibrational-rotational spectrum will be of the same type as that of a diatomic molecule. If, however, the vibration causes a change of dipole moment perpendicular to that axis, not only the frequencies $\nu_v + \nu_r$ and $\nu_v - \nu_r$ but also the pure vibration frequency ν_v will appear. The reason for this is that the change

in dipole moment now may have a component along the axis of rotation—the latter being always perpendicular to the molecular axis—and this component will not be influenced by the rotation.

In spherical-top molecules the vibrational-rotational spectrum is of the same type as that from linear molecules with a dipole change perpendicular to the axis of the molecule, since in both cases the change of dipole moment will be oriented at a random angle to the axis of rotation.

For symmetrical-top molecules the vibrational-rotational spectrum will be as simple as for the pure rotation if the change of dipole moment lies along the figure axis. If the change of dipole is perpendicular to this axis the rotation around the figure axis will influence the spectrum. Although this makes the spectrum more complicated, it also gives rise to the possibility of determining the moment of inertia around the figure axis. This cannot be done if only the pure rotational spectrum is known.

The vibrational-rotational spectra of asymmetric-top molecules are just as complicated as the corresponding pure rotational spectra.

THE RAMAN EFFECT

Polarizability

It has been shown that, while the polarizability of a molecule gives rise to Rayleigh scattering, *the changes of polarizability during intramolecular motions are responsible for the Raman effect*. However, before discussing the way in which polarizability is affected by various motions within the molecule, the polarizability itself must be described in more detail.

The simplest possibility is that the vector of the electric force induces a dipole moment in the molecule which is proportional to the electric vector and points in the same direction as this vector. Denoting the electric vector by $\vec{E}$, the dipole moment by $\vec{M}$ and the polarizability by α there results

$$(28) \quad \vec{M} = \alpha \vec{E}$$

In a more detailed way the same equation may be written

$$(29) \quad \begin{aligned} M_x &= \alpha E_x \\ M_y &= \alpha E_y \\ M_z &= \alpha E_z \end{aligned}$$

where E_x , E_y and E_z are the x , y and z components of the electric vector and M_x , M_y and M_z are similarly the components of $\vec{M}$.

The simple equation (29), however, cannot be expected to hold for the induced moment $\vec{M}$ unless one is dealing with the polarization of such symmetrical systems as a single atom, or as a tetrahedral molecule, *e. g.*,

methane and carbon tetrachloride, or as an octahedral molecule like sulfur hexafluoride. In general there will be some directions in which the molecules can be more easily polarized than in others. Moreover, the dipole moment will not point in the same direction as the electric vector, but it will instead tend to include a smaller angle with the direction of greater polarizability in the molecule.

But even in the general case the induced moment will be a linear function of the electric vector, yielding therefore the equation

$$(30) \quad \begin{aligned} M_x &= \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z \\ M_y &= \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z \\ M_z &= \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z \end{aligned}$$

where the coefficients α_{xx} , α_{xy} . . . are constants characteristic of the polarizability of the molecule, and are called the components of the polarizability. The polarizability itself will signify the whole system of the coefficients α_{xx} , α_{xy} , ... Such a system of coefficients establishing a linear relation between two vectors is called a tensor. Thus the polarizability is a tensor. The coefficients α_{xx} , α_{xy} are called the components of the tensor, just as the quantities M_x , M_y , M_z are called the components of the vector $\vec{M}$.

It will be noticed that equation (30) bears a similarity to equation (16). The displacements are substituted by the components of the electric vector, the forces by the components of the dipole moment, and the force constants a_{ik} by the components of the polarizability. This analogy extends so far that, corresponding to $a_{ik} = a_{ki}$, the relations

$$(31) \quad \alpha_{xy} = \alpha_{yx}, \quad \alpha_{yz} = \alpha_{zy}, \quad \alpha_{zx} = \alpha_{xz}$$

will hold. The way in which equation (31) can be proved is also quite similar to the procedure by which it has been shown that $a_{ik} = a_{ki}$. The starting point is that the quantities $\vec{E}$ and $\vec{M}$ are related to the electric energy of the polarized molecule as F and ζ have been related to the potential energy of the deformed molecule.

The analogy of the normal vibrations can also be found. In a normal vibration the force is pointing straight back into the equilibrium position. In a corresponding way electric vectors may be found for which $\vec{E}$ and $\vec{M}$ point in the same direction. Moreover, the orthogonality of normal vibrations will have its equivalent in the fact that there will always be three mutually perpendicular directions in the molecule for which $\vec{E}$ and $\vec{M}$ are parallel. If these three directions in the molecule are called ξ , η and ζ ,

and are used as the axes of a Cartesian coördinate system, one may write instead of (30)

$$(32) \quad \begin{aligned} M_{\xi} &= \alpha_{\xi} E_{\xi} \\ M_{\eta} &= \alpha_{\eta} E_{\eta} \\ M_{\zeta} &= \alpha_{\zeta} E_{\zeta} \end{aligned}$$

where M_{ξ} , M_{η} , M_{ζ} , E_{ξ} , E_{η} and E_{ζ} are the components of $\vec{M}$ and $\vec{E}$ in the directions ξ , η and ζ .

It is frequently of advantage to visualize the polarizability as an ellipsoid in a way similar to that by which a force or a dipole moment is frequently pictured, namely, by an arrow. Indeed, if one plots from a point all the dipole moments which are induced by unit electric forces pointing in all possible directions, the tops of the arrows representing the dipole moments will lie on an ellipsoid. The principal axes of this ellipsoid will have the lengths α_{ξ} , α_{η} and α_{ζ} and will point in the directions ξ , η and ζ . The ellipsoid has to be pictured as rigidly bound to the molecule just in the same way as the arrow representing the permanent dipole of a molecule must be considered as rigidly bound to it. The ellipsoid is called the polarizability ellipsoid.

It may happen that two axes, *e.g.*, α_{ξ} and α_{η} , have the same magnitude. Then the ellipsoid will become a rotational ellipsoid. Any direction in the ξ - η plane may be considered with equal justification as the principal axis, and the polarizability will be the same in all these directions. It will be noticed that there is here a close analogy to the twofold degenerate normal vibrations.

If all three axes, α_{ξ} , α_{η} and α_{ζ} , become equal, then instead of a polarizability ellipsoid there is a polarizability sphere. Any three orthogonal coördinates can be chosen as principal axes and for any of them equations (32) and (29) become identical. The analogy with a threefold degenerate vibration is evident.

The Depolarization Factor

If a molecule is fixed in space (which is the case for molecules in a crystal) the components of the polarizability can be measured in a direct way. For instance, the quantity α_{xy} may be obtained by irradiating the molecule with light polarized in the y direction and by observing the scattered light emitted in the z direction and polarized in the x direction. This is because light polarized in the y direction is defined as light in which the electric vector vibrates parallel to y , and a dipole moment vibrating along x will radiate in any direction perpendicular to x (and therefore also to z) light polarized in x .

One is concerned most frequently, however, with molecules oriented at

random. The polarization of the scattered radiation has then to be calculated by considering all positions of the scattering molecule and taking the average.

First consider a molecule with spherical polarizability, given by equation (29). If light polarized in the x direction falls on the molecule, the induced dipole is parallel to x , and the radiation scattered in any direction perpendicular to x is polarized along x .

If however the three axes of the polarizability are not the same, the induced moment will not be parallel to the direction in which the incident radiation is polarized. If then an incident radiation polarized along x is used and the observation is made from a direction perpendicular to x , the scattered light will not be completely polarized along x . It is then said that the scattered radiation is depolarized. The intensity of the scattered radiation polarized at right angles to x , divided by the intensity polarized parallel to x , is termed the depolarization factor. If the polarizability of the molecule is spherical the depolarization factor is zero. On the other hand, a depolarization factor equal to unity would mean that the scattered radiation is not polarized at all.

The discussion of the depolarization factor can be greatly simplified if the polarizability of the molecule is separated into two parts.

$$(33) \quad \begin{array}{lll} \alpha_{xx} = \alpha^s + \alpha_{xx}^a & \alpha_{xy} = \alpha_{xy}^a & \alpha_{xz} = \alpha_{xz}^a \\ \alpha_{yx} = \alpha_{yx}^a & \alpha_{yy} = \alpha^s + \alpha_{yy}^a & \alpha_{yz} = \alpha_{yz}^a \\ \alpha_{zx} = \alpha_{zx}^a & \alpha_{zy} = \alpha_{zy}^a & \alpha_{zz} = \alpha^s + \alpha_{zz}^a \end{array}$$

with

$$(34) \quad \alpha^s = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

The substance of equation (33) is that, instead of a polarizability with the components

$$\begin{array}{l} \alpha_{xx} \alpha_{xy} \alpha_{xz} \\ \alpha_{yx} \alpha_{yy} \alpha_{yz} \\ \alpha_{zx} \alpha_{zy} \alpha_{zz} \end{array}$$

two new polarizabilities may be considered,

$$(35) \quad \begin{array}{lll} \alpha_{xx}^a & \alpha_{xy}^a & \alpha_{xz}^a \\ \alpha_{yx}^a & \alpha_{yy}^a & \alpha_{yz}^a \\ \alpha_{zx}^a & \alpha_{zy}^a & \alpha_{zz}^a \end{array}$$

and

$$(36) \quad \begin{array}{lll} \alpha^s & 0 & 0 \\ 0 & \alpha^s & 0 \\ 0 & 0 & \alpha^s \end{array}$$

The induced moments are calculated separately for the polarizabilities [equations (35) and (36)], and then the results are added.

This means that one may also simply add the electric vectors radiated by the moments which would be obtained from equations (35) and (36) separately. It does not mean, in general, that the scattered intensities can be calculated with the help of the polarizabilities [(35) and (36)] separately, and the results then added. This is because the scattered intensities are proportional to the squares of the radiated electric vectors; and if, for instance, polarizabilities [(35) and (36)] should give rise to equal vectors and radiations in a certain direction, then together they would radiate the double value of the vector and the fourfold value of the intensity.

It can be shown, however, that if the special condition [equation (34)] is introduced, and if one takes the average value of the scattered intensities produced by molecules oriented at random in space, then the contributions of equations (35) and (36) to the scattered average intensities are simply additive. One can consider indeed the total scattering as *coming* from two distinct kinds of imaginary molecules. One kind possesses the polarizability (36), called the spherical part of the polarizability, and the other has the polarizability (35), called the anisotropic part of the polarizability.

The anisotropic part is a kind of polarizability no molecule could in reality possess. Indeed, it follows from equation (33) that

$$(37) \quad \alpha_{xx} + \alpha_{yy} + \alpha_{zz} = \alpha_{xx}^a + \alpha_{yy}^a + \alpha_{zz}^a + 3\alpha^s$$

and substituting (34) we have

$$(38) \quad \alpha_{xx}^a + \alpha_{yy}^a + \alpha_{zz}^a = 0.$$

Or, if a coordinate system is used having the principal axes ξ , η , ζ , we have $\alpha_\xi^a + \alpha_\eta^a + \alpha_\zeta^a = 0$. From this it follows that unless $\alpha_\xi^a = \alpha_\eta^a = \alpha_\zeta^a = 0$ at least one of these three quantities must be negative and that, therefore, in certain directions an electric vector would induce a moment which is oriented in a way opposite to the electric force. Though in a real molecule this never would happen, it is still of advantage to introduce these anisotropic polarizabilities since in the Raman effect they play an important role.

The spherical part of the polarizability will give rise to a scattering for which the depolarization factor is zero. For the anisotropic part, on the other hand, after averaging over the orientation of the molecules, the depolarization factor 3/4 is obtained. If the following relations are introduced:

$$(39) \quad (\alpha_{xx})^2 + (\alpha_{xx}^a)^2 + (\alpha_{xx}^s)^2 + (\alpha_{yy})^2 + (\alpha_{yy}^a)^2 + (\alpha_{yy}^s)^2 + (\alpha_{zz})^2 + (\alpha_{zz}^a)^2 + (\alpha_{zz}^s)^2 + (\alpha_{xy})^2 + (\alpha_{xy}^a)^2 + (\alpha_{xy}^s)^2 + (\alpha_{yz})^2 + (\alpha_{yz}^a)^2 + (\alpha_{yz}^s)^2 + (\alpha_{zx})^2 + (\alpha_{zx}^a)^2 + (\alpha_{zx}^s)^2 = |\alpha|^2$$

and $3(\alpha^s)^2 = |\alpha^s|^2$

then there is obtained for the depolarization factor D (frequently designated as ρ) the following relation:

$$(40) \quad D = \frac{3|\alpha^a|^2}{10|\alpha^s|^2 + 4|\alpha^a|^2}$$

Thus by measuring the depolarization factor one can get information about the relative magnitudes of the spherical and anisotropic parts of the polarizability. For the Rayleigh scattering of a molecule the depolarization factor is always small. If, for instance, it is assumed that in a given molecule the relative magnitudes of α_ξ , α_η and α_ζ are according to the ratio 2 : 1 : 1, then there is obtained

$$\frac{|\alpha^s|^2}{|\alpha^a|^2} = 8, \quad D = \frac{3}{84},$$

though the relative magnitudes chosen for α_ξ , α_η and α_ζ indicate a strong deviation of the spherical polarizability.

Instead of using polarized light for the incident radiation one may also use natural (unpolarized) light. On observing the scattered radiation at right angles to the incident beam it will again be found that spherical polarizability will give rise to totally polarized scattering. If, indeed, the incident beam arrives from the z direction then, since light is a "transverse vibration," only dipole moments in the x and y directions will be induced. If observation is now made along the y axis, the observed light can have electric vectors only in the x and z directions and, since there was no induced moment along z , the beam will be completely polarized in x .

For the anisotropic polarizability on the other hand it can be shown that if one irradiates from the direction z and observes from y , the intensities polarized in x and z will have the ratio 7 : 6. It is said, therefore, that the depolarization factor is 6/7. The general expression for D in case of unpolarized incident radiation is

$$(41) \quad D = \frac{6|\alpha^a|^2}{20|\alpha^s|^2 + 7|\alpha^a|^2}$$

The Rotational Raman Effect

If the polarizability of a molecule is not spherical, the induced moment will not depend on the electric force alone but also on the orientation of the molecule. Thus if the electric vector oscillates with the frequency of light and the molecule rotates, the scattered radiation will not consist exclusively of the same frequency as the incident light but will also contain sums and differences of the light frequency and rotational frequency. The scattered frequencies which are shifted from the incident frequencies by the rotational frequency, or by a multiple of the rotational frequency, are called the rotational Raman lines. From what has been said it follows that the anisotropic

part of the polarizability is alone responsible for the rotational Raman effect.

For a diatomic molecule and, in general, for a linear molecule, the polarizability will be represented by a rotational ellipsoid, the rotational axis of which coincides with the axis of the molecule. The rotation of the molecule will take place around an axis perpendicular to the molecular axis. Therefore, after turning through 180° , the molecular axis together with the rotation ellipsoid of the polarizability will return to its original position. During one complete period of rotation (360°) this will happen twice, and the polarizability will change therefore with a frequency which is twice as great as the frequency of rotation. Correspondingly in the rotational Raman effect, *twice* the rotation frequency has to be added to or subtracted from the incident frequency to get the position of the Raman lines.

Classically all rotational frequencies are possible and the rotational Raman effect should consist in a broadening of the Rayleigh scattering. According to quantum mechanics, however, only rotational frequencies satisfying equation (27) are allowed, and a number of equidistant Raman lines will appear. Their spacing will be, however, twice that found in the infrared spectrum.

Because of its low intensity and the proximity of the strong Rayleigh line, the rotational Raman effect is less easy to investigate than the vibrational rotational lines of the infrared spectrum. In some cases, it is nevertheless used to determine the moment of inertia. For instance, diatomic molecules consisting of two similar atoms (H_2 or N_2) do not have any infrared spectrum, although the Raman effect is present (or "active"). However, with poor resolution (which is frequently used to compensate for the low intensity when investigating light scattered from gases) the rotational Raman lines might be indistinguishable from the Rayleigh line. The intensity of the line into which Rayleigh line and rotational Raman lines merge can be obtained by setting all rotational frequencies and velocities equal to zero and considering the molecules at rest, but at random orientation in space. Usually this "line," which includes the lines of the rotational Raman effect, is called the Rayleigh line. The discussion in the previous section treating the scattering of molecules at random orientation had direct application to this Rayleigh "line." The remarks of this paragraph are of course also valid for nonlinear polyatomic molecules, the rotational Raman effect of which will now be discussed.

As a general rule the polarizability ellipsoid of a spherical-top molecule is itself spherical. Rotation does not affect it and no rotational Raman effect is to be expected.

The polarizability ellipsoid of a symmetrical-top molecule is usually a rotational ellipsoid with its rotational axis lying in the figure axis of the

molecule. Rotation around the figure axis should not be present, therefore, in the rotational Raman effect. The precession of the figure axis, on the other hand, affects the position of the polarizability ellipsoid and should give rise to frequency shifts in the scattering.

Since the axis around which the figure axis precesses can include any angle with the figure axis, the polarizability ellipsoid will not in general return to its original position after a precession of 180° . Therefore in the rotational Raman effect of the symmetrical-top molecule, not only the two-fold value of the precession frequency will appear, but also the precession frequency itself.

The rotational Raman spectrum of an asymmetrical-top molecule will be complicated. It will differ from the infrared rotational spectrum chiefly in the appearance of the twofold frequencies of molecular rotation. This is again due to the fact that an ellipsoid may regain its original position after having rotated through 180° .

The Vibrational Raman Effect

It has been shown in the general discussion of the Raman effect that if the polarizability of the molecule changes periodically in consequence of the vibration, then in the scattered radiation the sum and the difference of the incident frequency and the molecular vibration frequency will appear. If the vibrations of a polyatomic molecule are purely harmonic and if all components of the polarizability are strictly linear functions of the displacement, each vibration will contribute independently to the induced electric moment. As a consequence, each vibration may appear in the Raman effect, and the intensity with which such a frequency will be present may be judged by investigating the displacement belonging solely to the corresponding normal vibrations. The other normal vibrations need not be taken into account. Of course it may happen that the Raman line of a vibration has the intensity zero, that is, does not appear at all. Examples will be discussed later.

There is a fundamental difference between the *polarizability of the molecule* (giving rise to the Rayleigh scattering) and the *change in polarizability during a vibration*, which will be discussed next. If both are written in the coordinate system of the principal axes one obtains

$$(32) \quad \begin{aligned} M_\xi &= \alpha_\xi E_\xi \\ M_\eta &= \alpha_\eta E_\eta \\ M_\zeta &= \alpha_\zeta E_\zeta \end{aligned}$$

and

$$(42) \quad \begin{aligned} M_{\xi'} &= \Delta\alpha_\xi E_{\xi'} \\ M_{\eta'} &= \Delta\alpha_\eta E_{\eta'} \\ M_{\zeta'} &= \Delta\alpha_\zeta E_{\zeta'} \end{aligned}$$

where equations (32) and (42) give the components of the induced moment brought about by the polarizability and change of polarizability respectively; $\Delta\alpha_{\xi'}$, $\Delta\alpha_{\eta'}$ and $\Delta\alpha_{\zeta'}$ are the principal axes of the change of polarizability. The coördinates ξ' , η' and ζ' in which the axes of the change of polarizability point, are distinguished from ξ and η and ζ by dashes or primes, since it is not necessary that the axes of the polarizability and those of the changes of polarizability should point in the same direction. Now, as has already been indicated, α_{ξ} , α_{η} and α_{ζ} must be positive, since it is impossible for an electric force to create in a molecule a dipole moment pointing in the opposite direction. On the other hand, there is no reason why $\Delta\alpha_{\xi}$, $\Delta\alpha_{\eta}$ or $\Delta\alpha_{\zeta}$ should not be negative. After all, these quantities signify changes of polarizability which may be either positive, corresponding to an increase of polarizability, or negative, corresponding to a decrease.

From this it follows that the change of polarizability may be purely anisotropic, that is, not containing any spherical part at all. Indeed this will be the rule for all vibrations which change the symmetry of the molecule.

The reason for this rule is as follows. The spherical part of the polarizability is characterized by one single quantity α^* . Now any such simple quantity must have for the symmetrical configuration of the molecule a maximum or minimum with regard to those degrees of freedom which are orthogonal to all the completely symmetrical displacements of the molecule. This argument is indeed a familiar one when applied to a molecule possessing a plane of symmetry. The potential energy is then expected to have a maximum or minimum in the symmetrical configuration. It is to be emphasized that it is the *linear* change of polarizability which gives rise to the simple vibrational Raman effect. In a maximum or minimum the quantity α^* as a first approximation will remain unchanged, and its linear change with the displacement is exactly zero. But the statement just now made, that α^* does not change with displacements destroying the symmetry, and the statement it is desired to prove, namely, that the change of polarizability caused by such displacements has no spherical part, $\Delta\alpha^*$, mean exactly the same thing.

With the same kind of reasoning it cannot be shown that the anisotropic part of the change of polarizability is zero for vibrations which change the molecular symmetry. This anisotropic part cannot be characterized by a single number, and the various components may change linearly with such vibrations without violating the requirements of symmetry. This will become clearer by considering an example.

In Figure 7 is shown a model of a vibration of the acetylene molecule, C_2H_2 . The full and empty circles give the equilibrium positions of the two carbon and two hydrogen atoms. All the equilibrium positions lie on a

straight line, giving the molecule axial symmetry. The arrows indicate a vibration which destroys the axial symmetry. The full ellipse is a cross-section of the polarizability ellipsoid for the equilibrium position. The dotted ellipse gives the ellipsoid for the displaced position, although the amount of the displacement is deliberately exaggerated for the sake of clarity. There is

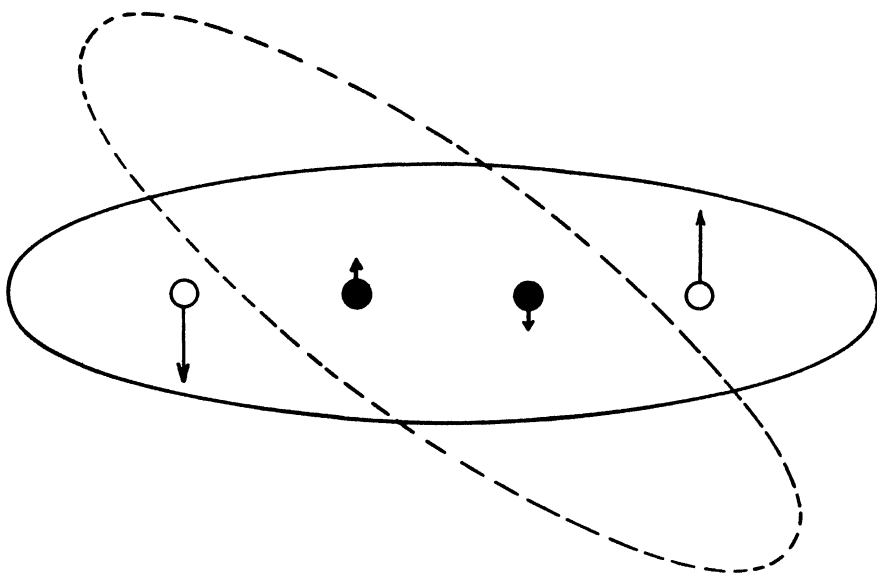


FIGURE 7. The Polarizability Ellipsoid for the Equilibrium and Displaced Positions.

no reason why the ellipsoid should not turn, and therefore change, with the vibration in the manner indicated in the figure. But at the same time not only

$$\alpha^s = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3},$$

but even the three quantities α_{xx} , α_{yy} and α_{zz} (the polarizabilities parallel and perpendicular to the molecular axis) will have a maximum or minimum at the equilibrium position.

The rule that $\Delta\alpha^s$ vanishes for vibrations which destroy the symmetry leads to the conclusion that for such vibrations the depolarization coefficient, ρ , must be $3/4$ if the primary radiation has been linearly polarized, or $6/7$ if it is not polarized. This enables one to distinguish the vibrations which do not destroy the molecular symmetry from those which do so, since the former as a general rule will have smaller depolarization factors, (*i.e.*, $\rho \approx 0$).

In addition to the fundamental vibrations in the Raman effect, for which

the frequency of a normal vibration has to be added or subtracted from the frequency of the incident radiation, there are also overtones and combination tones. These have the same reasons for appearing as have the overtones and combination tones in infrared absorption, namely, mechanical and electrical anharmonicity. The latter means, in the case of the Raman effect, terms of a quadratic, or higher, order, in the dependence of the polarizability on the displacements.

The same qualitative rules mentioned in the discussion of the infrared spectrum hold for the relative intensities of overtones and combination tones in the Raman effect; but, because of the weakness even of the "strong" fundamentals in the Raman effect, only relatively few overtones and combination tones are observed. It should be mentioned, however, that whereas many fundamentals have an intensity exactly equal to zero, all first overtones should be present in the Raman effect even though their intensity is very small.

The Vibrational-Rotational Raman Effect

If the change of polarizability during a vibration is not spherical, then it will be affected by rotation and the vibrational lines will probably have a rotational structure. For vibrations which do not change the molecular symmetry this rotational structure will be similar to that accompanying the Rayleigh line. For vibrations which do change the molecular symmetry the rotational structure should be particularly pronounced, because the change of polarizability is purely anisotropic for such vibrations and is influenced strongly by the change in molecular orientation. In such a vibrational-rotational band, frequencies may appear which are not present in the purely rotational Raman effect. Thus the rotational frequency of a spherical-top molecule may be observed as well as the frequency of rotation around the figure axis in a symmetrical-top molecule. Moreover in a linear molecule the simple rotational frequency might appear, although in the purely rotational spectrum only the double value of this frequency is present.

When the vibrational-rotational Raman effect is observed with poor resolution, one obtains a simple line which may be interpreted as arising from molecules at random orientation having negligibly small velocities and frequencies of rotation.

Chapter 5

Determination of the Number and Character of Normal Vibrations and of Raman Frequencies in Polyatomic Molecules

The Symmetrical Linear Molecule ABA

If the atoms of the symmetrical linear molecule ABA are displaced in the manner indicated in Figure 8, where the B atom remains at rest and the two A atoms are moved toward B by the same amounts, then no force will act on B, while on the two A atoms there will act equal forces each pointing

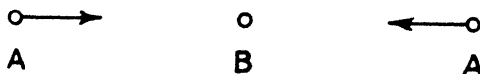


FIGURE 8. The Totally Symmetrical Vibration of the Symmetrical Linear Molecule ABA (*e.g.*, Carbon Dioxide).

straight back into the equilibrium positions of the A atoms. The displacement pictured in Figure 8 belongs, therefore, to a normal vibration. During this normal vibration the symmetry of the molecule is entirely preserved. The vibration therefore is called totally symmetrical to distinguish it from other vibrations which leave only certain elements of symmetry undisturbed. The latter vibrations are then called symmetrical with regard to certain symmetry elements. The unqualified word *symmetrical* will be used, in general, to mean *totally* symmetrical.

If all the atoms are displaced along the molecular axis, all forces will lie along this axis. To find the normal vibrations along the axis it is necessary only to find the particular displacements which will give rise to forces proportional to the displacements multiplied by the masses. Thus the vibrations along the axis can be discussed without reference to the other normal vibrations.

For the symmetrical molecule BA_2 the normal vibrations can be found without reference to the forces. The argument that all normal vibrations have to be orthogonal to one another and also to the “vibrations” with zero frequency—the translations and rotations—will be used repeatedly.

The molecule possesses three degrees of freedom along the axis. Three normal vibrations must correspond to them. Figure 8 gives one, the

translation along the axis gives another, and the third vibration is completely defined by the requirement that it should be orthogonal to the two mentioned above. The two atoms A must be displaced by equal amounts in the same direction in order that this vibration may be orthogonal to the symmetrical vibration. If it is likewise to be orthogonal to the translation, the atom B must be displaced in a direction opposite to atoms A; and the ratio of the displacement of B to the displacement of the two atoms A must be $2M_A : M_B$, where M_A and M_B are the masses of A and B. This vibration is given qualitatively in Figure 9. It will be noticed that if this picture is

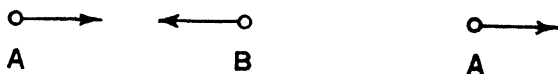


FIGURE 9. The Antisymmetrical Vibration of the Symmetrical Linear Molecule ABA.

reflected in a plane vertical to the axis and passing through B, all displacements will be inverted, *i.e.*, they are all multiplied by -1 . Such a vibration is called antisymmetrical with regard to this plane. It may also be said that it is antisymmetrical with regard to reflection in the point of equilibrium of B, which is the center of symmetry of the molecule.

On the other hand, the picture remains unchanged if it is turned around the axis of the molecule. The vibration is, therefore, symmetrical with regard to this axis. A vibration which is antisymmetrical with regard to some symmetry operations is called an antisymmetrical vibration, even though it is symmetrical with regard to other elements of symmetry.

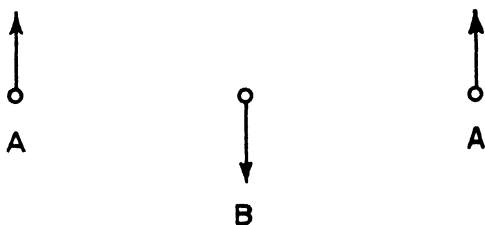


FIGURE 10. The Doubly Degenerate "Deformation" Vibration of the Symmetrical Linear Molecule ABA.

All degrees of freedom belonging to displacements which lie in a plane must be considered. Six such displacements and six vibrations should occur in the plane. Three of them are the linear vibrations, namely, the symmetrical and the antisymmetrical vibrations and the translation along the axis. Two more are given by the translation in the plane perpendicular to the molecular axis and by the rotation around an axis perpendicular to the plane. It is apparent that the vibration shown in Figure 10 is the only

one which is lying in the plane of the paper and is orthogonal to all the five displacements mentioned above. In this figure all the displacements are perpendicular to the molecular axis. The displacements of the two A atoms are equal, and the ratio of the B displacement to an A displacement is again $2M_A:M_B$.

A vibration similar to the one just given can be found in a direction perpendicular to the plane of the paper or in any direction perpendicular to the molecular axis. All these vibrations have the same frequencies, because they differ from one another only in their direction in space. They can be transformed into one another by rotation around the molecular axis, which yields a degenerate vibration. The degeneracy is twofold, as all other vibrations may be obtained by superposition of the vibration in the plane of the paper and the one perpendicular to this plane.

The reason for the degeneracy just described is the axial symmetry of the molecule. In fact the reason for all degeneracy is, as a rule, the symmetry of the molecule, because otherwise no two normal vibrations would have exactly the same frequency.

The degenerate vibration is symmetrical in respect to a reflection in the plane perpendicular to the molecular axis and passing through the equilibrium position of B. It is antisymmetrical in respect to the center of symmetry, *i.e.*, in respect to reflection in the equilibrium position of B. The vibration is called degenerate rather than symmetrical or antisymmetrical, even though it is symmetrical in respect to some symmetry elements and antisymmetrical in respect to others.

Three possible types of vibration have been discussed: symmetrical, antisymmetrical and degenerate. A molecule which has *no* symmetry at all has *only symmetrical vibrations*, since a vibration is called symmetrical as long as it does not destroy any symmetry elements. Only molecules with a rather high degree of symmetry have degenerate vibrations. As a general rule linear molecules and symmetrical-top molecules have twofold degenerate vibrations, whereas spherical-top molecules have two and threefold degenerate vibrations. If two or more frequencies are very nearly equal, although the symmetry of the molecule does not require them to be the same, this is termed an accidental degeneracy. If, on the other hand, the degeneracy is due to symmetry, it is called a necessary degeneracy.

The linear molecule BA_2 should have $3 \times 3 - 5 = 4$ normal vibrations. Of the three possible types of vibration, *i.e.*, symmetrical, antisymmetrical and degenerate, the last-named has to be counted twice; consequently all the vibrations have been found without reference to interatomic forces. The molecular symmetry, together with the orthogonality relation, completely determine the form of the normal vibrations. This is possible in this case because each vibration differs from the others in its symmetry

properties. In other molecules in which more than one vibration has the same symmetry type it will be necessary to consider the forces in order to establish the exact shape of the vibrations.

The next point to consider is which of the vibrations just found will be present in the infrared spectrum and which in the Raman effect.

The symmetrical vibration evidently cannot cause a change of the dipole moment and consequently it cannot be found in the infrared spectrum. On the other hand, there is no reason why the polarizability should not change during this vibration. One should expect, therefore, to find the symmetrical vibration in the Raman effect.

For the antisymmetrical and degenerate vibrations a change of dipole moment is possible, for the former type in the direction of the molecular axis, and for the latter perpendicular to it. Thus both types of vibration are to be expected in the infrared spectrum and may be distinguished with the help of their different rotational structures. For the antisymmetrical vibration only those lines should be present which include the rotational frequency, whereas in the case of the degenerate vibration, the pure vibrational frequency should be observed in addition to the rotational structure.

It is not difficult to see that during the antisymmetrical vibration there can be no linear change of the polarizability. If, for example, all the displacements shown in Figure 9 are reversed, a configuration is obtained which is the original one reflected in the center of symmetry. Such a reflection does not change the polarizability ellipsoid and therefore the same polarizability belongs to opposite elongations of the antisymmetrical vibrations. This means that the polarizability cannot depend on the first power of the antisymmetrical displacement, and the antisymmetrical vibration does not appear in the Raman effect. The polarizability may depend, however, on the square of the displacement of the antisymmetrical vibration, since such a dependence is not in contradiction with the fact that the polarizability has the same value for opposite displacements. Thus the first overtone of the antisymmetrical vibration may be present in the Raman effect; but like all overtones it will be weak.

The same statements can be made about the change of polarizability which takes place during the degenerate vibration as have been made for the antisymmetrical vibration. This is true because the degenerate vibration is antisymmetrical with regard to reflection in the center of symmetry. Indeed no vibration can appear in the Raman effect which is antisymmetrical to the center of symmetry of the molecule. It will be remembered that the center of symmetry of a molecule is a point from which equal vectors of opposite direction lead to pairs of equal atoms. These atoms are called the reflections of each other in the center of symmetry. Not all molecules have a center of symmetry and in its absence the above does

not apply. On the other hand, vibrations which are symmetrical with regard to the center of symmetry cannot cause a change of dipole moment and cannot appear in the infrared spectrum. This is because the atoms remain in a configuration which is symmetrical to the center in this type of vibration, and hence any direction and the opposite direction will be equivalent. As will be seen in subsequent examples for all molecules which have a center of symmetry, each vibration has to be either symmetrical or antisymmetrical with regard to this center. Thus if a center of symmetry is present, no vibration can appear in both the Raman effect and the infrared spectrum.

Although the form of the normal vibrations and the question whether they may appear in the infrared and the Raman spectrum can be decided without reference to the magnitude of the elastic forces, the value of the frequencies is in direct connection with the forces. The correct procedure would be to start from experimental data and calculate all the force constants (a_{ik}) of the molecule. For a symmetrical molecule BA_2 enough data are available to effect this as soon as the fundamental frequencies in the infrared and Raman spectra are known.

In general the known experimental data are too few to calculate all elastic constants of the molecule. One may make simple assumptions, however, which greatly reduce the number of force constants to be determined, and then calculate these fewer constants from the experimental data. Of course the simplifying assumptions are not exactly correct, and they frequently lead to a direct contradiction of the observations. Nevertheless they may often provide a qualitative idea of the frequencies and may even be used to predict spectra in a very rough way.

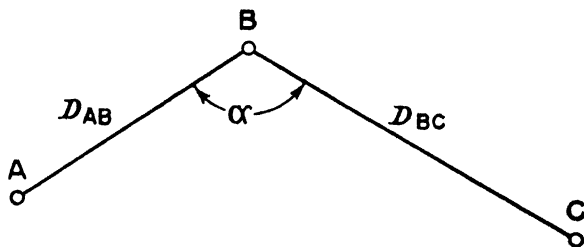


FIGURE 11. The Valence Force Model of the Unsymmetrical Nonlinear Molecule ABC (Chlorocyanide). The AB and BC distances are designated by D_{AB} and D_{BC} , respectively, and the valence angle by α .

One of these simplifying assumptions about the elastic forces is obtained by introducing the valence force model. The valences are drawn between neighboring atoms according to the structural formula of the molecule, and it is assumed that elastic forces arise because of the change in valence

length and valence angle during a vibration. Thus if a valence length is stretched by dl , the two atoms linked by the valence are pulled together by a force $-kdl$, where k is the force constant of the valence in question. If on the other hand we have three atoms A, B and C as pictured in Figure 11, where AB and BC are linked by valence bonds making the valence angle α at B, then a change of α during vibration will produce forces at the atoms A and C. These forces will be perpendicular to the lines joining AB and CB respectively, and their magnitude will be $\frac{K}{D_{AB}} d\alpha$, and $\frac{K}{D_{BC}} d\alpha$, where K is the force constant of the angle, and D_{AB} and D_{BC} are the distances between AB and BC. A force will also be acting on B, and it can be obtained from those acting on A and on C by considering that the sum of the three forces must be zero.

Applying this model to the symmetrical vibration of BA_2 (Figure 8), it is found that a displacement dx of A will produce a change of valence length $dl = dx$ and a force $-kdl = -kdx$ acting on the same atom. Using the simple formula for the harmonic vibration, the frequency of the symmetrical vibration is found to be $\frac{1}{2\pi} \sqrt{\frac{k}{M_A}}$ [cf. equation (7)].

For the antisymmetrical vibration, a displacement of A by dx is accompanied by a displacement of B by $-\frac{2M_A}{M_B} dx$ and therefore by a change of the valence length by $-\frac{2M_A + M_B}{M_B} dx$. Therefore the force $\frac{2M_A + M_B}{M_B} kdx$ will act on A. The resulting frequency will be equivalent to $\frac{1}{2\pi} \sqrt{\frac{k(2M_A + M_B)}{M_A M_B}}$ and the ratio of the frequencies of antisymmetrical and symmetrical vibrations will become $\sqrt{\frac{2M_A + M_B}{M_B}}$. Since this ratio should depend only on the masses M_A and M_B it gives a good possibility of checking the valence force model.

For the degenerate vibration a displacement dy of A will be accompanied by a displacement $-\frac{2M_A}{M_B} dy$ of B and by a change $d\alpha = 2 \frac{2M_A + M_B}{M_B} \cdot \frac{dy}{D_{AB}}$ of the ABA angle. This angle is, of course, 180° for the equilibrium position. Here D_{AB} is the distance AB. Thus the force $-\frac{(4M_A + 2M_B)K}{M_B D_{AB}^2} dy$ will act on A and the frequency found will correspond to

$$\frac{1}{2\pi} \sqrt{\frac{K(4M_A + 2M_B)}{M_A M_B D_{AB}^2}}.$$

Frequently a different model called the central force model is used to calculate the frequencies. In this model forces act between the atoms along the lines joining them. These forces depend on the interatomic distances. For the equilibrium configuration they do not necessarily vanish but only balance each other. For small displacements from the equilibrium configuration they can be considered as linear functions of the changes of distance. In this model the angles in the equilibrium configuration are not stabilized by specific angle forces, but rather by forces acting between second neighbors. For more complicated molecules, more constants often appear in this model than can be evaluated. The plausible assumption is made, therefore, that forces acting between atoms lying at some distance apart can be neglected.

There is no general rule as to when one should apply the valence force model, when the central force model and when, and to what extent, both models may be expected to break down. One would expect, however, that if small atoms, such as hydrogen atoms, are attached to a bigger central atom, then valence forces will stabilize the angle with the central atom and the valence force model will be better. If large atoms, for example iodine atoms, are attached to a smaller central atom such as carbon, the direct action between the atoms is the more important and the central force system is better. Of course the validity of such statements is at least as questionable as the models themselves.

Applying the central force model to the symmetrical linear BA_2 molecule, it may be assumed that the force $K_{AB} - k'_{AB}dD_{AB}$ acts between A and B, where dD_{AB} is the change of the AB distance brought about by the vibration. Similarly $K_{AA} - k'_{AA}dD_{AA}$ should act between A and A, dD_{AA} being the change of this distance.* For the equilibrium position these forces should cancel and it follows therefore that $K_{AB} + K_{AA} = 0$.

For the symmetrical vibration the displacement dx of the atom A will give rise to $dD_{AB} = dx$ and $dD_{AA} = 2dx$. The force $-(k'_{AB} + 2k'_{AA})dx$ will act therefore on A and the frequency $\frac{1}{2\pi}\sqrt{\frac{k_{AB} + 2k_{AA}}{M_A}}$ will be obtained.

For the antisymmetrical vibration a displacement dx of A will correspond to $dD_{AB} = \frac{2M_A + M_B}{M_B}dx$ and $dD_{AA} = 0$. Hence the force

$-\frac{2M_A + M_B}{M_B}k'_{AB}dx$, and the frequency $\frac{1}{2\pi}\sqrt{\frac{k'_{AB}(2M_A + M_B)}{M_A M_B}}$ is obtained.

For the degenerate vibrations the AA and AB distances do not change.

* The dashes or primes introduced in k_{AB} and k_{AA} distinguish these force constants from the similar force constants in the valence force model. In the present example one may leave the dashes out without causing confusion. In later examples this will be impossible.

The line connecting the two A atoms also retains its direction but the AB line becomes inclined. Thus, while the components of K_{AB} and K_{AA} still compensate each other in the direction of the molecular axis, K_{AB} will have an uncompensated component perpendicular to the axis. If A has been displaced by dy , the magnitude of this uncompensated component will be $K_{AB} \frac{2M_A + M_B}{M_B} \cdot \frac{dy}{D_{AB}}$. Thus there is obtained the frequency for the degenerate vibration, namely, $\frac{1}{2\pi} \sqrt{-\frac{K_{AB}(2M_A + M_B)}{M_A M_B D_{AB}}}$. If a real value for this frequency is desired, the quantity under the radical must be positive. This means that K_{AB} must be negative, corresponding to attraction between A and B. Since it is known that $K_{AB} + K_{AA} = 0$, it follows that K_{AA} will be positive and the two A atoms will repel each other. If K_{AB} were positive it would be found that the force $K_{AB} \cdot \frac{2M_A + M_B}{M_B} \cdot \frac{dy}{D_{AB}}$ acting on A during a degenerate vibration would be positive, *i. e.*, it would tend to increase the displacement, and the equilibrium in the linear configuration would not be stable.

In general the ratio predicted by the valence force model for the frequencies of the symmetrical and antisymmetrical vibrations is not far from the ratio found experimentally. In terms of the central force model this means that k'_{AA} is small compared to k'_{AB} . The frequency of the degenerate vibration is usually much smaller than that of the antisymmetric vibration. It follows that, according to the valence force model, $\frac{2K}{D_{AB}^2}$ must be small compared to k or, according to the central force model, $\frac{K_{AB}}{D_{AB}}$ is small compared to k'_{AB} .

The Linear Molecule ABC

Not only molecules consisting actually of three different atoms, such as hydrogen cyanide, HCN, but also molecules like nitrous oxide, N_2O , which contain two similar atoms in unlike positions, belong to this class. In fact the properties of the central nitrogen atom and the nitrogen atom at the end of the molecule in nitrous oxide are as different as though they were different kinds of atoms. It may be considered that one has a valence of 5, the other a valence of 3, and that near one there is a concentration of positive charge and near the other a concentration of negative charge. In fact only those atoms have the same properties within a molecule which, in addition to being chemically identical, are also in symmetrical positions. If a rotation or reflection of the molecule will lead to the same configuration

as the original one, then atoms interchanged by this symmetry must behave identically.

The vibrations along the molecular axis will be discussed first. There are again three degrees of freedom corresponding to the displacements dx_A , dx_B and dx_C of the three atoms. One of the "normal vibrations" is the translation along the axis. For the two remaining vibrations the orthogonality relation $M_A dx_A + M_B dx_B + M_C dx_C = 0$ must hold. Thus the displacement of the central atom in terms of the displacements of the other two atoms can be expressed by:

$$(43) \quad dx_B = - \frac{M_A dx_A + M_C dx_C}{M_B}$$

Apart from this relation no detailed statement can be made about the form of these normal vibrations without taking the forces into account. It is evident that the linear vibrations do not disturb the axial symmetry of the molecule and they are therefore symmetrical vibrations. There is no reason why the dipole moment and polarizability should not change during these vibrations, and thus both vibrations may be expected to appear in the infrared and Raman spectra.

In order to find the approximate form and frequency which the vibrations may be expected to have, the valence force model is introduced. The force constants acting between AB and BC will be called k_{AB} and k_{BC} .

The calculations will be simplified if the changes of the distances D_{AB} and D_{BC} are introduced instead of the displacements of A, B and C. If D_{AB} is changed by dD_{AB} then the accelerations of A and B will be $-\frac{k_{AB}dD_{AB}}{M_A}$ and $\frac{k_{AB}dD_{AB}}{M_B}$. The second derivative of D_{AB} will thus be

$$(44) \quad \frac{d^2 D_{AB}}{dT^2} = -k_{AB}dD_{AB} \left(\frac{1}{M_A} + \frac{1}{M_B} \right).$$

On introducing into equation (44) the reduced mass M_{AB} [identical with μ cf. equation (7)] in the following manner,

$$(45) \quad \frac{1}{M_{AB}} = \frac{1}{M_A} + \frac{1}{M_B}$$

there is obtained the relation

$$(46) \quad \frac{d^2 D_{AB}}{dT^2} = - \frac{k_{AB}dD_{AB}}{M_{AB}}.$$

If the third atom C were not present this equation would be correct in the present form and the familiar expression $\nu_{AB} = \frac{1}{2\pi} \sqrt{\frac{k_{AB}}{M_{AB}}}$ would result for

the frequency of the AB molecule. Similarly if only B and C were present there would be obtained

$$(47) \quad \frac{d^2 D_{BC}}{dT^2} = - \frac{k_{BC} dD_{BC}}{M_{BC}}$$

and, as shown above, the expression

$$(48) \quad \nu_{BC} = \frac{1}{2\pi} \sqrt{\frac{k_{BC}}{M_{BC}}}$$

relating the frequency, force and mass.

However the stretching is not the only cause giving rise to a second derivative of D_{AB} . If dD_{BC} is different from zero, B will have the acceleration $-\frac{k_{BC} dD_{BC}}{M_B}$ and the amount $\frac{k_{BC} dD_{BC}}{M_B}$ must be added to $\frac{d^2 D_{AB}}{dT^2}$. A similar statement holds with respect to the effect of dD_{AB} on $\frac{d^2 D_{BC}}{dT^2}$. The following complete equations of motion then result.

$$(49) \quad \frac{d^2 D_{AB}}{dT^2} = - \frac{k_{AB} dD_{AB}}{M_{AB}} + \frac{k_{BC} dD_{BC}}{M_B}$$

$$(50) \quad \frac{d^2 D_{BC}}{dT^2} = \frac{k_{AB} dD_{AB}}{M_B} - \frac{k_{BC} dD_{BC}}{M_{BC}}$$

For a normal vibration with the frequency ν one finds also that

$$(51) \quad D_{AB} = D_{AB}^0 \sin 2\pi \nu t \quad \text{and} \quad D_{BC} = D_{BC}^0 \sin 2\pi \nu t$$

with D_{AB}^0 and D_{BC}^0 designating the amplitudes of D_{AB} and D_{BC} . Substituting into the equations of motion given above the following expression results:

$$(52) \quad -4\pi^2 \nu^2 D_{AB}^0 = - \frac{k_{AB}}{M_{AB}} D_{AB}^0 + \frac{k_{BC}}{M_B} D_{BC}^0$$

$$(53) \quad -4\pi^2 \nu^2 D_{BC}^0 = \frac{k_{AB}}{M_B} D_{AB}^0 - \frac{k_{BC}}{M_{BC}} D_{BC}^0$$

This system of equations has a solution different from $D_{AB}^0 = D_{BC}^0 = 0$ only if its determinant vanishes, thus:

$$(54) \quad \begin{vmatrix} -\frac{k_{AB}}{M_{AB}} + 4\pi^2 \nu^2 & \frac{k_{BC}}{M_B} \\ \frac{k_{AB}}{M_B} & -\frac{k_{BC}}{M_{BC}} + 4\pi^2 \nu^2 \end{vmatrix} = 0$$

$$(4\pi^2 \nu^2)^2 - \left(\frac{k_{AB}}{M_{AB}} + \frac{k_{BC}}{M_{BC}} \right) 4\pi^2 \nu^2 + \frac{k_{AB} k_{BC}}{M_{AB} M_{BC}} - \frac{k_{AB} k_{BC}}{M_B^2} = 0.$$

The two solutions of this quadratic equation give the two frequencies desired:

$$(55) \quad 4\pi^2\nu^2 = \frac{k_{AB}}{2M_{AB}} + \frac{k_{BC}}{2M_{BC}} \pm \sqrt{\left(\frac{k_{AB}}{2M_{AB}} - \frac{k_{BC}}{2M_{BC}}\right)^2 + \frac{k_{AB}k_{BC}}{M_B^2}}.$$

If it were not for the term $k_{AB}k_{BC}/M_B^2$ under the radical sign these could be written

$$(56) \quad \nu_{AB} = \frac{1}{2\pi} \sqrt{\frac{k_{AB}}{M_{AB}}} \quad \text{and} \quad \nu_{BC} = \frac{1}{2\pi} \sqrt{\frac{k_{BC}}{M_{BC}}}$$

i. e., the frequencies of the independent molecules AB and BC. The term $\frac{k_{AB}k_{BC}}{M_B^2}$ is responsible, therefore, for the coupling of these two oscillations. Its effect is to make the higher of the two frequencies ν_{AB} and ν_{BC} higher and the lower of the two frequencies still lower. If, however $M_B(\nu_{AB}^2 - \nu_{BC}^2) \gg 2(M_{AB}M_{BC})^{1/2}\nu_{AB}\nu_{BC}$ then the influence of coupling is negligible.

This situation is characteristic of the normal vibrations of a polyatomic molecule in a general way, and its study is useful in order to obtain a qualitative picture of the vibration of more complicated molecules. If the vibrations of two smaller groups in a big molecule are found, and if the fact is taken into account that because the two groups are parts of the same molecule their vibrations will be coupled, then the effect of the coupling will be to lower the frequency of the slower vibration and to increase the frequency of the faster vibration. The effect of the coupling will be, of course, greater if the coupling itself is greater, and it will also be greater if the difference between the two original frequencies is small. For the molecule ABC, coupling increases as the mass M_B decreases, because the coupling acts through the atom B and will be great if this atom can be accelerated readily by virtue of its small mass.

When the central force model is applied to the molecule ABC, there are obtained the forces

$$K_{AB} - k'_{AB}dD_{AB}, \quad K_{BC} - k'_{BC}dD_{BC} \quad \text{and} \quad K_{AC} - k'_{AC}dD_{AC}$$

acting between AB, BC and AC. The equilibrium condition necessitates that $K_{AB} = K_{BC} = -K_{AC}$. The equations of motion then will be

$$(57) \quad \frac{d^2D_{AB}}{dT^2} = -\left(\frac{k'_{AB}}{M_{AB}} + \frac{k'_{AC}}{M_A}\right)dD_{AB} + \left(\frac{k'_{BC}}{M_B} - \frac{k'_{AC}}{M_A}\right)dD_{BC}$$

$$(58) \quad \frac{d^2D_{BC}}{dT^2} = \left(\frac{k'_{AB}}{M_B} - \frac{k'_{AC}}{M_C}\right)dD_{AB} - \left(\frac{k'_{BC}}{M_{BC}} + \frac{k'_{AC}}{M_C}\right)dD_{BC}$$

and there will result the frequencies shown below.

$$(59) \quad 4\pi^2\nu^2 = \frac{k'_{AB}}{2M_{AB}} + \frac{k'_{BC}}{2M_{BC}} + \frac{k'_{AC}}{2M_{AC}} = A, \text{ where}$$

$$A = \sqrt{\left(\frac{k'_{AB}}{2M_{AB}} + \frac{k'_{BC}}{2M_{BC}} + \frac{k'_{AC}}{2M_{AC}}\right)^2 - \frac{M_A + M_B + M_C}{M_A M_B M_C} (k'_{AB}k'_{BC} + k'_{BC}k'_{AC} + k'_{AC}k'_{AB})}$$

and where M_{AC} is defined by $\frac{1}{M_{AC}} = \frac{1}{M_A} + \frac{1}{M_C}$.

To find the remaining frequencies of the ABC molecule the possible displacements in a plane will be discussed. Six degrees of freedom must then be considered as leading to six vibrations. Of these, five are given by the two translations in the plane, the rotation around the axis perpendicular to the plane, and the two vibrations along the molecular axis. There is only one vibration orthogonal to all these five motions. In this vibration, as can be easily verified, all atoms move perpendicularly to the molecular axis and the relative amplitudes of the atoms A, B and C will be

$$M_C D_{BC}, \quad -\frac{M_A M_C D_{AC}}{M_B} \quad \text{and} \quad M_A D_{AB}.$$

Such a vibration will be possible in any direction perpendicular to the molecular axis and therefore is degenerate. It will be noticed that it was possible to find the form of motion of this degenerate vibration. This is because it is the only one of its symmetry type for the ABC molecule.

During the degenerate vibration both the dipole moment and the polarizability may change, and this vibration should appear both in the infrared spectrum and in the Raman effect. However, the spherical part of the polarizability remains unchanged. Indeed the change of polarizability is of the same type as the one shown in Figure 7. The depolarization factor in the Raman effect is therefore 3/4 or $\approx 6/7$, depending on whether the incident light is polarized or unpolarized.

The frequency of the degenerate vibration is, according to the valence force model,

$$(60) \quad \frac{1}{2\pi} \sqrt{K \frac{M_A M_B D_{AB}^2 + M_B M_C D_{BC}^2 + M_A M_C D_{AC}^2}{M_A M_B M_C D_{AB}^2 D_{BC}^2}}$$

where K is the force constant of the angle ABC.

According to the central force model, the frequency will be

$$(61) \quad \frac{1}{2\pi} \sqrt{K_{AC} \frac{M_A M_B D_{AB}^2 + M_B M_C D_{BC}^2 + M_A M_C D_{AC}^2}{M_A M_B M_C D_{AB} D_{BC} D_{AC}}}$$

The Symmetrical Linear Molecule ABBA

The most important molecule of this type is acetylene.

The molecule must have $3 \times 4 - 5 = 7$ vibrational degrees of freedom. Figure 12 gives a qualitative picture of the vibrations.

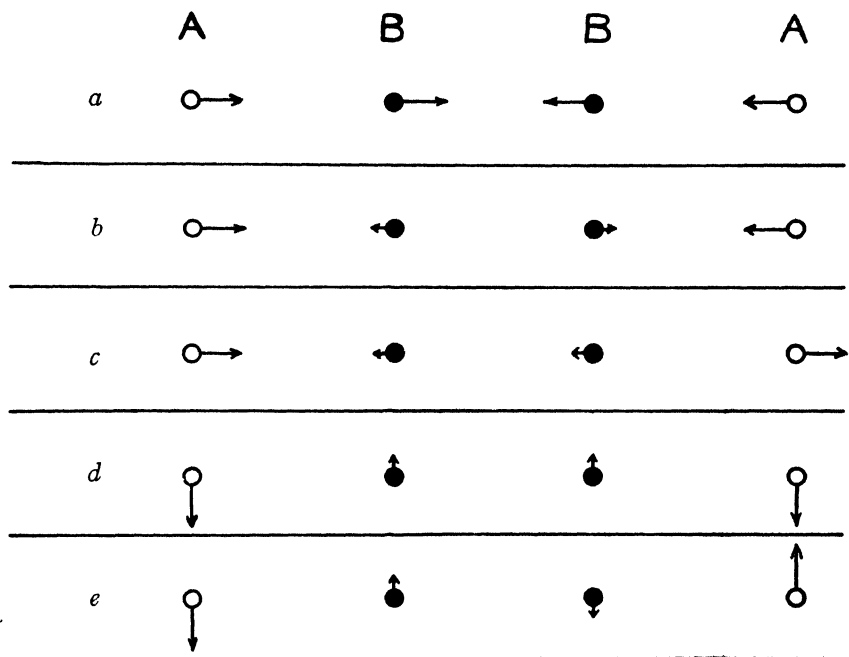


FIGURE 12. The Vibrations of the Symmetrical Linear Molecule ABBA (Acetylene). The vibrations designated by *a*, *b*, and *e* are present in the Raman Effect and those by *c* and *d* are present in infrared absorption.

The vibrations in rows *a* and *b* are symmetrical, that in row *c* is antisymmetrical and those in *d* and *e* are twofold degenerate, giving all together seven degrees of freedom. The form of the two symmetrical vibrations cannot be determined without a knowledge of the forces since we have here two vibrations not differing in their symmetry. The actual forms of vibrations drawn in Figure 12 are approximately those to be expected for acetylene. In one of them it is mainly the BB distance that is changing, in the other mainly the AB distance.

The antisymmetrical vibration is the only one of its kind and its form of vibration can therefore be predicted. The ratio of the displacements of A and B is $-\frac{M_B}{M_A}$. The displacements lie, of course, along the axis.

The two degenerate vibrations differ in their symmetry properties. The vibration in row *d* is symmetrical to the plane perpendicular to the molecular axis and passing through the center of the line BB at the symmetry center of the molecule. The vibration, however, is antisymmetrical with regard to reflection in the center of symmetry. The vibration in row *e* is antisymmetrical to the plane described above, but symmetrical to the center of symmetry.

Since the two degenerate vibrations differ in their symmetry each of them is the only one in its symmetry class, and their form can be predicted. The displacements are, of course, perpendicular to the molecular axis. For the vibration in row *d* the ratio of displacements of A and B is $-\frac{M_B}{M_A}$. For the vibration in row *e*, the ratio of displacements of two neighboring atoms A and B is $-M_B D_{BB}/M_A D_{AA}$.

The presence of a center of symmetry prevents a vibration from being present in both infrared and Raman effect. A brief consideration shows that only the antisymmetrical vibration and the degenerate vibration which is antisymmetric to the center of symmetry can appear in the infrared, while all other vibrations can be present in the Raman effect. The degenerate vibration which is symmetrical to the symmetry center should have a depolarization factor $3/4$ or $\approx 6/7$. It has not been observed from acetylene. It seems to be a general rule, not explained by theory, that vibrations in which mainly the hydrogen atoms are moving, and in which the valence distances remain unchanged, either are not observed in the Raman effect or have a rather small intensity.

The frequencies obtainable from the valence force model will now be calculated. If again k_{AB} and k_{BB} are denoted as the valence force constants of the bonds AB and BB, and K as the force constant of the angle, the two frequencies of the symmetrical vibrations will then be given by the equation

$$(62) \quad 4\pi^2\nu^2 = \frac{k_{AB}}{2M_{AB}} + \frac{k_{BB}}{M_B} \pm \sqrt{\left(\frac{k_{AB}}{2M_{AB}} + \frac{k_{BB}}{M_B}\right)^2 - 2\frac{k_{AB}k_{BB}}{M_A M_B}}$$

where again $\frac{1}{M_{AB}} = \frac{1}{M_A} + \frac{1}{M_B}$ has been introduced. The two signs relate to the two frequencies.

The antisymmetrical frequency is obtained from the equation

$$(63) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k_{AB}}{M_{AB}}}$$

and the frequency of the degenerate vibration, which is antisymmetrical to the center of symmetry, is given by

$$(64) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{K}{M_{AB} D_{AB}^2}}$$

where D_{AB} is the distance from an A atom to the nearest B atom.

The frequency of the other degenerate frequency, symmetrical to the center of symmetry, may be denoted by

$$(65) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{K(M_A D_{AA}^2 + M_B D_{BB}^2)}{M_A M_B D_{AB}^2 D_{BB}^2}}$$

Thus the frequency ratio of the degenerate vibration antisymmetrical to the center of symmetry, to the degenerate vibration symmetrical to the center of symmetry is given by

$$\sqrt{\frac{(M_A + M_B) D_{BB}^2}{M_A D_{AA}^2 + M_B D_{BB}^2}}$$

(The first of the vibrations mentioned above should appear in the infrared and the second in the Raman effect.) This ratio is smaller than unity since $D_{AA} > D_{BB}$, but for acetylene it is experimentally greater than unity. In this case the vibration which is antisymmetrical to the center is obtained directly from the infrared spectrum. The second degenerate vibration is calculated from a combination tone in the infrared spectrum. For the central force model the situation is essentially the same, as will be seen. This shows that both the valence force model and the central force model, being only rough approximations, lead in this case to incorrect predictions.

In the central force model the force acting between the two B atoms will be denoted by $K_{BB} - k'_{BB} d D_{BB}$, the force acting between an A atom and the B atom nearest to it by $K_{AB} - k'_{AB} d D_{AB}$, and the force acting between an A atom and the B atom farthest from it by $K_{AB'} - k'_{AB'} d D_{AB'}$, (where $D_{AB'} = D_{BB} + D_{AB}$). Between the two A atoms no force will be assumed. Indeed the central force model would become too complicated and its usefulness would cease if forces between distant atoms were included, although difficulty concerning the frequency ratio of the degenerate vibration could be eliminated by introducing forces between the two A atoms.

The equilibrium condition requires $\frac{1}{2} K_{BB} = K_{AB} = -K_{AB'}$. The two symmetrical vibrations will be given by

$$(66) \quad 4\pi^2 \nu^2 = \frac{k'_{AB} + k'_{AB'}}{2M_{AB}} + \frac{k'_{BB}}{M_B} = \sqrt{\left(\frac{k'_{AB} + k'_{AB'}}{2M_{AB}} + \frac{k'_{BB}}{M_B}\right)^2 - \frac{4k'_{AB}k'_{AB'} + 2k'_{BB}(k'_{AB} + k'_{AB'})}{M_A M_B}}$$

The frequency of the antisymmetrical vibration is found from the equation

$$(67) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k'_{AB} + k'_{AB'}}{M_{AB}}}$$

while the frequency of the degenerate vibration, which is antisymmetrical to the center is given by

$$(68) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{K_{AB} \cdot D_{BB}}{D_{AB} D_{AB} \cdot M_{AB}}}$$

and, finally, the frequency of degenerate vibration, symmetrical to the center, can be calculated from

$$(69) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{K_{AB} \cdot (M_A D_{AA}^2 + M_B D_{BB}^2)}{M_A M_B D_{AB} D_{BB} D_{AB}'}}$$

It will be noticed that the last two frequencies have the same ratio as occurs in the valence force model.

The Nonlinear Symmetrical Molecule BA₂

Typical representatives of this group are water and sulfur dioxide.

The molecule BA₂ has three vibrational degrees of freedom. Two of these, which are symmetrical, are shown qualitatively for water in Figures 13*a* and 13*b*. The third, shown in Figure 13*c*, is an antisymmetrical vibration. It can be seen that it is antisymmetrical to a plane passing through B and perpendicular to the AA line. Inasmuch as this vibration is the only one of its symmetry type, its form can be predicted from the forces alone. The two atoms will vibrate with equal amplitude and opposite phases toward and away from the equilibrium position of B. The atom B vibrates on a line parallel to AA, but the amplitude of its vibration must be such that the center of gravity does not move during the vibration. The forms of the two symmetrical vibrations depend on the assumptions made about the forces acting in the molecule.

All the vibrations may appear both in the infrared spectrum and the Raman effect. In the symmetrical vibrations the change of dipole moment during the vibration is perpendicular to AA, and in the antisymmetrical vibration it is parallel to this line, resulting in a difference in the rotational structure. In the Raman effect the antisymmetrical vibration must have a depolarization factor of 3/4 (or $\approx 6/7$).

Molecules of this class are generally asymmetrical-top molecules and their rotational spectra are very complicated.

In order to calculate the vibrational frequencies, first the valence force model will be assumed. Then the force $-k_{AB}dD_{AB}$ will act on the A atom parallel to the A—B bond, when that bond is stretched, and $-\frac{K}{D_{AB}}d\alpha$ will act perpendicularly to the bond if the angle is changed (cf. Figure 13*b*). The antisymmetrical vibration will then have the frequency

$$(70) \quad \nu = \frac{1}{2\pi} \sqrt{k_{AB} \left(\frac{1}{M_A} + \frac{1 - \cos \alpha}{M_B} \right)}.$$

The two symmetrical frequencies may be obtained from the expression

$$(71) \quad 4\pi^2\nu^2 = \frac{k_{AB}}{2} \left(\frac{1}{M_A} + \frac{1 + \cos \alpha}{M_B} \right) + \frac{K}{D_{AB}^2} \left(\frac{1}{M_A} + \frac{1 - \cos \alpha}{M_B} \right) = A, \text{ where}$$

$$A = \sqrt{\left[\frac{k_{AB}}{2} \left(\frac{1}{M_A} + \frac{1 + \cos \alpha}{M_B} \right) - \frac{K}{D_{AB}^2} \left(\frac{1}{M_A} + \frac{1 - \cos \alpha}{M_B} \right) \right]^2 + 2 \frac{K}{D_{AB}^2} k_{AB} \frac{\sin^2 \alpha}{M_B^2}},$$

by using the positive and negative sign respectively.

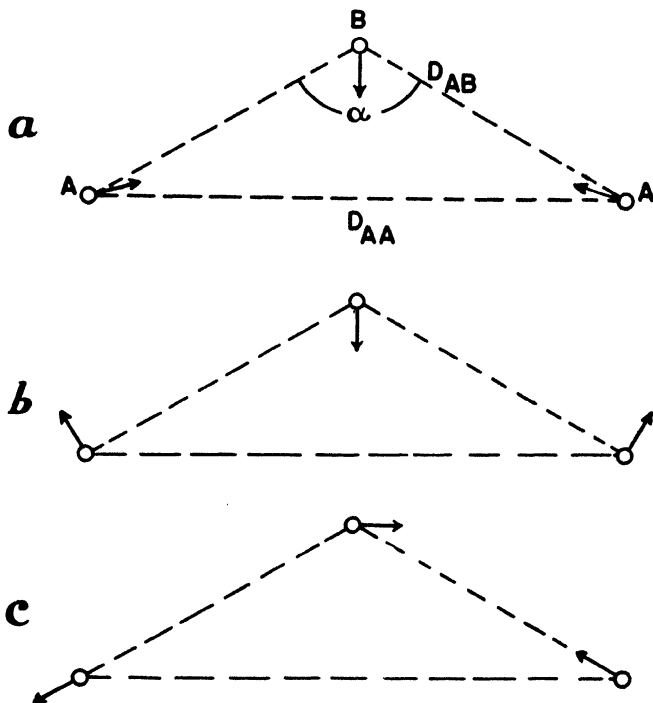


FIGURE 13. The Vibrations of the Nonlinear Symmetrical Molecule BA_2 (Water). All three vibrations are present in both infrared absorption and the Raman Effect.

If $k_{AB} \gg \frac{K}{D_{AB}^2}$ (which is satisfied in all analyzed cases)* one may write for the two symmetrical vibrations the approximate frequencies:

*The fact that $k_{AB} \gg \frac{K}{D_{AB}^2}$ is not sufficient if $M_B \ll M_A$. Similar restrictions should be made in later applications, an example of which is carbon tetraiodide, CI_4 .

$$(72) \quad \nu = \frac{1}{2\pi} \sqrt{k_{AB} \left(\frac{1}{M_A} + \frac{1 + \cos \alpha}{M_B} \right)} \quad \text{and}$$

$$(73) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{2K}{D_{AB}^2 M_A} \frac{M_B + 2M_A}{M_B + M_A(1 + \cos \alpha)}}$$

The first of these depends on the valence force constant alone, whereas the second contains only the angle force constant K . Moreover it may be stated, as a first approximation, that in only one of these two vibrations does the valence distance change while in the other only the valence angle changes. These vibrations are termed the valence and deformation vibrations respectively. The valence vibration for water is shown in Figure 13a and the deformation vibration in 13b.

The distinction between the two kinds or types of vibration is even less rigorous than the valence force model itself. For linear molecules a rigorous distinction can be made: the nondegenerate vibrations are the valence vibrations and the degenerate ones are deformation vibrations. The antisymmetric vibration may be considered as a valence vibration. For $M_B \gg M_A$ or $\alpha \approx 90^\circ$ this frequency should be nearly the same as that of the symmetrical valence vibration. For complicated molecules these concepts may be applied in a rather rough but, at the same time, helpful way. As a general rule the deformation vibrations have smaller frequencies than the corresponding valence vibrations, the ratio often attaining a value of 1:2.

In the central force model the equilibrium conditions required that the forces K_{AB} and K_{AA} vanish if the atoms are in equilibrium positions. If the atoms are displaced the forces $-k'_{AB}dD_{AB}$ and $-k'_{AA}dD_{AA}$ will act along AB and AA and the frequency of the antisymmetrical vibration will be given by

$$(74) \quad \nu = \frac{1}{2\pi} \sqrt{k'_{AB} \left(\frac{1}{M_A} + \frac{1 - \cos \alpha}{M_B} \right)}$$

The symmetrical frequencies may be obtained from the expression

$$(75) \quad 4\pi^2\nu^2 = \frac{k'_{AB}}{2} \left(\frac{1}{M_A} + \frac{1 + \cos \alpha}{M_B} \right) + \frac{k'_{AA}}{M_A} \neq A, \text{ where}$$

$$A = \sqrt{\left[\frac{k'_{AB}}{2} \left(\frac{1}{M_A} + \frac{1 + \cos \alpha}{M_B} \right) - \frac{k'_{AA}}{M_A} \right]^2 + k'_{AA}k'_{AB} \left(\frac{1 - \cos \alpha}{M_A^2} \right)}.$$

It will be noticed that these frequencies do not become identical with the frequencies of the linear molecule A_2B if one sets $\alpha = 180^\circ$. This is due to the fact that the equilibrium condition in this case does not require $K_{AB} - K_{AA} = 0$. When $k'_{AA} \ll k'_{AB}$ roughly two frequencies are obtained,

$$(76) \quad \nu = \frac{1}{2\pi} \sqrt{k'_{AB} \left(\frac{1}{M_A} + \frac{1 + \cos \alpha}{M_B} \right)} \quad \text{and} \quad \nu = \frac{1}{2\pi} \sqrt{\frac{K'_{AA}(2M_A + M_B)(1 + \cos \alpha)}{M_A[M_A(1 + \cos \alpha) + M_B]}}$$

which have properties similar to those of the valence and deformation vibrations. If, in addition $M_B \gg M_A$ or $\alpha \approx 90^\circ$, the first of these frequencies should be approximately the same as the antisymmetrical frequency.

From the three observed frequencies of the nonlinear BA_2 molecule the constants k_{AB} , $\frac{K}{D^2_{AB}}$ and α (on the basis of the valence force model) or the constants k'_{AB} , k'_{AA} and α (on the basis of the central force model) have often been calculated. The results for the valence angle α which are obtained from these two models often differ quite markedly from each other and are, at best, only approximate even when there are valid reasons for preferring one model to the other.

The Symmetrical Plane Molecule BA_3

The chief representatives of this group are ions such as the carbonate or nitrate ions, $[\text{CO}_3]^-$ and $[\text{NO}_3]^-$, occurring in solutions as crystals. Since the forces between the molecules change to rather a small extent during an intramolecular vibration, these ions behave, as a first approximation, independently of the neighboring atoms.

The BA_3 molecule has six vibrational degrees of freedom. The vibrations are shown qualitatively in Figure 14. The vibration 14a is symmetrical. In 14b the crosses mean a displacement of the A atoms at right angles to the molecular plane and pointing upward. The circle around atom B means a similar displacement downward. Thus a vibration is obtained which is antisymmetrical to the plane of the molecule. The symmetrical and antisymmetrical vibrations are the only ones of their symmetry type and their form is therefore uniquely determined.

Figures 14c and 14d show two degenerate vibrations. That they are degenerate can be seen from the fact that by rotating the molecule through an angle of 120° around the B atom one may obtain new vibrations. Both vibrations 14c and 14d have a twofold degeneracy, thus bringing the number of vibrations to the required six.

The antisymmetrical and the degenerate vibrations may be expected in the infrared spectrum. In the Raman effect the symmetrical and the degenerate frequencies will be present. The latter will have a depolarization factor, $3/4$ or $\approx 6/7$.

If the valence force model is used in the way it has been used previously (*i. e.*, so that the forces produced are proportional to the change in the AB distance, dD_{AB} , and the ABA angle, $d\alpha$), then it is found that the frequency of the antisymmetrical vibration is zero. This amounts practically to a

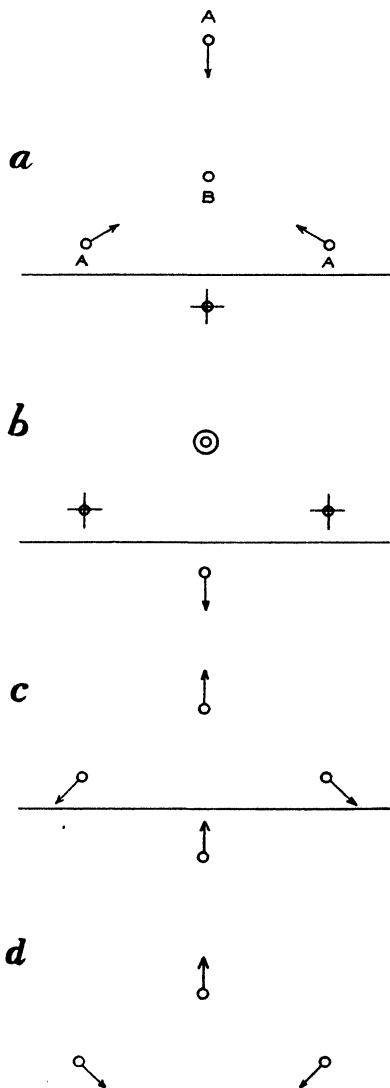


FIGURE 14.

The Vibrations of the Symmetrical Plane Molecule BA_3 [Nitrate Ion, $(NO_3)^-$].

lack of stability for the plane structure. Therefore a further angle force $-\frac{\bar{K}}{D_{AB}} d\beta$ acting on A, perpendicularly to the molecular plane will be introduced, where $d\beta$ is the angle which the line A_1B includes during a vibration with the BA_3 plane. The forces acting on B may then be calculated from the requirement that the sum of the restoring forces acting on the molecule may be zero.

The symmetrical vibration frequency is obtained from the following equation:

$$(77) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k_{AB}}{M_A}},$$

the antisymmetrical vibration frequency from:

$$(78) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{(3 + 2\sqrt{3})K}{D_{AB}^2} \left(\frac{1}{3M_A} + \frac{1}{M_B} \right)}$$

and the two degenerate vibrations from:

$$(79) \quad 4\pi^2\nu^2 = \frac{1}{2} \left(k_{AB} + \frac{3K}{D_{AB}^2} \right) \left(\frac{1}{M_A} + \frac{3}{2M_B} \right) \\ \pm \sqrt{\frac{1}{4} \left(k_{AB} - \frac{3K}{D_{AB}^2} \right)^2 \left(\frac{1}{M_A} + \frac{3}{2M_B} \right)^2 + \frac{27}{4} k_{AB} \cdot \frac{K}{D_{AB}^2} \cdot \frac{1}{M_B}}.$$

If $\frac{K}{D_{AB}^2} \ll k_{AB}$, there is obtained a symmetrical valence vibration (Figure 14c) and a degenerate antisymmetrical deformation vibration (Figure 14d).

In the central force model the equilibrium condition requires

$$(80) \quad K_{AB} = -\sqrt{3} K_{AA}.$$

The three expected frequencies can then be calculated from the following equations:

$$(81) \text{ for the symmetrical vibration: } \nu = \frac{1}{2\pi} \sqrt{\frac{k'_{AB} + 3k'_{AA}}{M_A}}$$

$$(82) \text{ for the antisymmetrical vibration: } \nu = \frac{1}{2\pi} \sqrt{\frac{-K_{AB}}{D_{AB}}} \left(\frac{1}{M_A} + \frac{3}{M_B} \right)$$

(K_{AB} is again called positive if it is a repulsion, and negative if it is an attraction; only in the latter case is the plane structure stable) and for the degenerate vibrations:

$$(83) \quad 4\pi^2\nu^2 = \frac{1}{2} k'_{AB} \left(\frac{1}{M_A} + \frac{3}{2M_B} \right) + \frac{3k'_{AA}}{4M_A} - \frac{3K_{AB}}{4D_{AB}} \left(\frac{1}{3M_A} + \frac{1}{M_B} \right) \pm A$$

$$A = \sqrt{\left[\frac{1}{2} k'_{AB} \left(\frac{1}{M_A} + \frac{3}{2M_B} \right) - \frac{3k'_{AA}}{4M_A} + \frac{3K_{AB}}{4D_{AB}} \left(\frac{1}{3M_A} - \frac{1}{M_B} \right) \right]^2} \\ + \frac{1}{4M_A} \left(k'_{AB} + \frac{K_{AB}}{D_{AB}} \right) \left(\frac{3k'_{AA}}{M_A} + \frac{K_{AB}}{M_A D_{AB}} + \frac{6K_{AB}}{M_B D_{AB}} \right)$$

In this case both k'_{AA} and $\frac{K_{AB}}{D_{AB}}$ must necessarily be small compared to k'_{AB} in order that valence and angle vibrations should represent reasonable approximations to the actual vibrations.

The Symmetrical Plane Molecule A_2BC

A typical example is formaldehyde, H_2CO .

These molecules differ from the BA_3 type in that one of the three A atoms is different and consequently, the threefold symmetry is destroyed. A plane of symmetry remains which passes through B and C and is perpendicular to AA. Another plane of symmetry is, of course, the plane of the molecule itself.

There are three symmetrical vibrations (Figures 15*a,b,c* give them qualitatively for formaldehyde) and three antisymmetrical vibrations (Figures 15*d,e,f*). Two of the latter are antisymmetrical to the plane perpendicular to AA (Figure 15*d,e*) and one (Figure 15*f*) is antisymmetrical to the plane of the molecule. All vibrations may appear in the infrared and in the Raman effect. The antisymmetrical vibrations should have the depolarization factor $3/4$ or $\approx 6/7$.

Since there are three vibrations of the same symmetry type the explicit expressions for the frequencies become rather complicated. They will be discussed qualitatively.

As a first approximation the BA_2 and the BC groups may be considered separately. The former will have two symmetrical vibrations, of which one can be considered frequently as a valence vibration and the other as a deformation vibration. The vibration of BC will be, of course, a valence vibration.

As a second approximation the vibrations of the two groups must necessarily be coupled because, for example, a BA_2 vibration will cause a motion of B which will affect the BC vibration. The coupling will be small if M_B is large compared with the other masses. However, if the ABA angle is greater than 90° the BC vibration (Figure 15*c*) will be more strongly coupled to the deformation vibration (Figure 15*b*). The effect of the coupling between two frequencies will be the greater, the closer together the two frequencies lie originally. An example of this occurred in considering the linear ABC molecules. It will be remembered that coupling has the effect of raising the higher and reducing the lower of two interacting frequencies. If two frequencies were originally nearly the same and the coupling causes a "splitting," then the two resulting vibrations will be rather different from the two original ones. If, for instance, the BC vibration and the BA_2 deformation vibration originally had similar frequencies, then in each of the resulting vibrations both the BC distance and the ABA angle

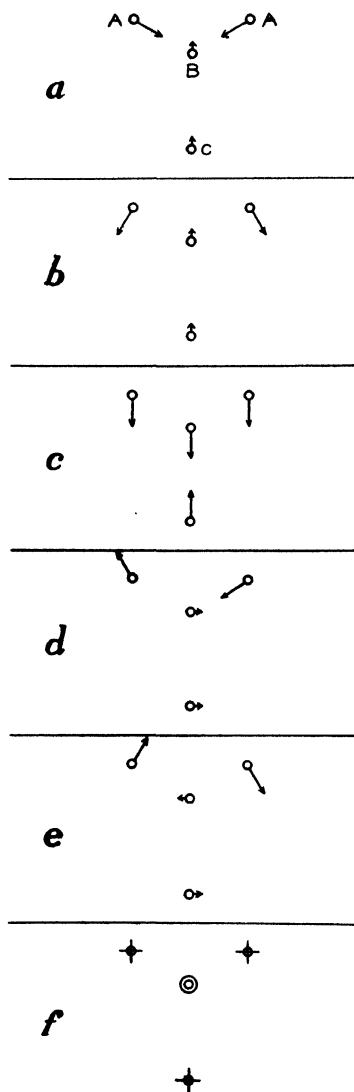


FIGURE 15.

The Vibrations of the Plane Symmetrical Molecule A₂BC (Formaldehyde). All the vibrations are present in both infrared absorption and the Raman Effect. A difference in arrow length indicates a difference in the magnitude of the atom's displacement.

will change: in one vibration both will simultaneously increase or decrease, whereas in the other, one will increase and the other decrease. It is to be noted that a valence vibration may be often as slow as a deformation vibration if heavy masses are involved in the former.

Of the two vibrations which are antisymmetrical to the plane perpendicular to AA, one is usually a valence vibration (15*d*) and the other a

deformation vibration (15e). The vibration which is antisymmetrical to the plane of the molecule (15f) is also a deformation vibration.

If $M_B \gg M_A$ one may expect the two valence vibrations shown in Figures 15a and 15d to have almost the same frequencies. The third valence vibration (15c) will be different, because a different valence has been stretched. The three deformation frequencies will differ also because different angle forces are involved in them. In Figure 15b it is essentially the ABA angle which will be changed, whereas in 15e it is the ABC angle. In Figure 15f a similar angle force comes into action, the constant of which has been denoted for the BA_3 molecule by $\bar{K}$.

The Symmetrical Pyramidal Molecule BA_3

An example of this type of molecule is ammonia, NH_3 . This compound has two symmetrical and two twofold degenerate vibrations corresponding in all to six vibrational degrees of freedom. All the vibrations may be expected both in the infrared spectrum and in the Raman effect and the depolarization factor for the two degenerate frequencies is $3/4$ or $\approx 6/7$.

For the symmetrical frequencies in the valence force model the following relationship is obtainable:

$$(84) \quad 4\pi^2\nu^2 = \frac{k_{AB}}{2} \left[\frac{1}{M_A} + \frac{1+2\cos\alpha}{M_B} \right] + \frac{K}{D_{AB}^2} \frac{1+2\cos\alpha}{1+\cos\alpha} \left[\frac{1}{M_A} + \frac{2(1-\cos\alpha)}{M_B} \right] \pm A,$$

$$A = \sqrt{\left\{ \frac{k_{AB}}{2} \left[\frac{1}{M_A} + \frac{1+2\cos\alpha}{M_B} \right] - \frac{K}{D_{AB}^2} \frac{1+2\cos\alpha}{1+\cos\alpha} \left[\frac{1}{M_A} + \frac{2(1-\cos\alpha)}{M_B} \right] \right\}^2 + 4k_{AB} \frac{K}{D_{AB}^2} \frac{(1+2\cos\alpha)^2}{(1+\cos\alpha)} \frac{(1-\cos\alpha)}{M_B^2}}.$$

Here α is the ABA angle and K is the constant of the angle-force arising from a change in α . An analog to $\bar{K}$, which was used for the plane BA_3 molecule, has not been introduced, since without assuming such a force the stability of the molecule can be assured. As a consequence the previous and the following formulas will correspond for $\alpha=120^\circ$ to the frequencies of the plane BA_3 molecule only if in the latter $\bar{K}=0$ is introduced.

For the degenerate frequencies there is obtained

$$(85) \quad 4\pi^2\nu^2 = \frac{k_{AB}}{2} \left[\frac{1}{M_A} + \frac{1-\cos\alpha}{M_B} \right] + \frac{K}{2D_{AB}^2(1+\cos\alpha)} \left[\frac{2+\cos\alpha}{M_A} + \frac{(1-\cos\alpha)^2}{M_B} \right] \pm A$$

$$A = \sqrt{\left\{ \frac{k_{AB}}{2} \left[\frac{1}{M_A} + \frac{1-\cos\alpha}{M_B} \right] - \frac{K}{2D_{AB}^2(1+\cos\alpha)} \left[\frac{2+\cos\alpha}{M_A} + \frac{(1-\cos\alpha)^2}{M_B} \right] \right\}^2 + \frac{k_{AB}K(1-\cos\alpha)^3}{M_B^2 D_{AB}^2 (1+\cos\alpha)}}.$$

It will be seen that, for $k_{AB} \gg \frac{K}{D_{AB}^2}$, valence and deformation vibrations can be distinguished. More specifically there will be a symmetrical valence vibration, a symmetrical deformation vibration, a degenerate valence vibration and a degenerate deformation vibration. For $M_B \gg M_A$ the two valence vibrations will have only slightly differing frequencies.

In the central force model the equilibrium conditions require $K_{AB} = K_{AA} = 0$. As a consequence the following formulas will become identical for $\alpha \approx 120^\circ$ with those of the plane BA_3 molecule only if in the latter is set $K_{AB} = K_{AA} = 0$.

For the symmetrical vibrations this leads to the equation

$$(86) \quad 4\pi^2\nu^2 = \frac{k'_{AB}}{2} \left[\frac{1}{M_A} + \frac{1+2\cos\alpha}{M_B} \right] + \frac{3k'_{AA}}{2M_A} \\ \pm \sqrt{\left\{ \frac{k'_{AB}}{2} \left[\frac{1}{M_A} + \frac{1+2\cos\alpha}{M_B} \right] - \frac{3k'_{AA}}{2M_A} \right\}^2 + \frac{2k'_{AA}k'_{AB}(1-\cos\alpha)}{M_A^2}}$$

and for the degenerate vibrations to the equation

$$(87) \quad 4\pi^2\nu^2 = \frac{k'_{AB}}{2} \left[\frac{1}{M_A} + \frac{1-\cos\alpha}{M_B} \right] + \frac{3k'_{AA}}{4M_A} \\ \pm \sqrt{\left\{ \frac{k'_{AB}}{2} \left[\frac{1}{M_A} + \frac{1-\cos\alpha}{M_B} \right] - \frac{3k'_{AA}}{4M_A} \right\}^2 + \frac{k'_{AA}k'_{AB}(1-\cos\alpha)}{2M_A^2}}$$

When $k'_{AB} \gg k'_{AA}$ valence and deformation vibrations can be distinguished. The molecules of this group have the rotational structures of symmetrical-top molecules.

The Tetrahedral Molecule BA_4

Examples of this type of molecule are seen in methane, CH_4 , and carbon tetrachloride, CCl_4 . These molecules have nine vibrational degrees of freedom, of which one is symmetrical, one twofold degenerate and two threefold degenerate.

In the infrared spectrum only the two threefold degenerate vibrations are present, but in the Raman effect all vibrations are to be expected. The depolarization factor of the degenerate vibrations is $3/4$ or $\approx 6/7$. For the symmetrical vibrations the change of polarizability is spherical and consequently the depolarization factor is zero. This vibration has, moreover, no rotational structure and it should appear as a sharp line. The rotational structure of the other lines is that corresponding to a spherical-top.

In the valence force model it is only necessary to introduce the constants

k_{AB} and K , connected with the change of the AB distance and the ABA angle. The symmetrical vibration can then be calculated from

$$(88) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k_{AB}}{M_A}},$$

and the frequency of the twofold degenerate vibration from:

$$(89) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{3K}{D_{AB}^2 M_A}}$$

and the two threefold degenerate from:

$$(90) \quad 4\pi^2\nu^2 = \frac{k_{AB}}{2} \left(\frac{1}{M_A} + \frac{4}{3M_B} \right) + \frac{K}{D_{AB}^2} \left(\frac{1}{M_A} + \frac{8}{3M_B} \right) \\ \pm \sqrt{\left[\frac{k_{AB}}{2} \left(\frac{1}{M_A} + \frac{4}{3M_B} \right) - \frac{K}{D_{AB}^2} \left(\frac{1}{M_A} + \frac{8}{3M_B} \right) \right]^2 + \frac{Kk_{AB}}{D_{AB}^2} \left(\frac{8}{3M_B} \right)^2}.$$

The symmetrical vibration is a valence vibration. It consists of all A atoms moving simultaneously toward and away from B. The twofold degenerate vibration is a deformation vibration, the B atom remaining at rest and the A atoms moving strictly perpendicular to the AB bonds.

If $k_{AB} \gg \frac{K}{D_{AB}^2}$, one of the two threefold degenerate vibrations will be a

valence and the other a deformation vibration. As has been mentioned, however, the condition $k_{AB} \gg \frac{K}{D_{AB}^2}$ is not always sufficient if $M_A \gg M_B$.

Thus for tetraiodomethane, CI_4 , the distinction between valence and deformation frequencies is certainly wrong and for carbon tetrachloride, CCl_4 , its application is of doubtful value. For $M_B \gg M_A$ the two valence vibrations (one of which is symmetrical and the other threefold degenerate) should have similar frequencies.

In the central force model the equilibrium conditions require

$$(91) \quad K_{AB} = -\sqrt{6} K_{AA}.$$

The equation then for the symmetrical frequency will be

$$(92) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k'_{AB} + 4k'_{AA}}{M_A}}$$

and for the twofold degenerate frequency

$$(93) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k'_{AA} D_{AA} + K_{AA}}{M_A D_{AA}}}$$

and for the threefold degenerate vibrations

$$(94) \quad 4\pi^2\nu^2 = \frac{k'_{AB}}{2} \left(\frac{1}{M_A} + \frac{4}{3M_B} \right) + \frac{k'_{AA}}{M_A} - \frac{K_{AB}}{D_{AB}} \left(\frac{1}{4M_A} + \frac{4}{3M_B} \right) \pm A,$$

$$A = \sqrt{\left\{ \frac{k'_{AB}}{2} \left(\frac{1}{M_A} + \frac{4}{3M_B} \right) - \frac{k'_{AA}}{M_A} + \frac{K_{AB}}{D_{AB}} \left(\frac{1}{4M_A} - \frac{4}{3M_B} \right) \right\}^2 + \frac{4 \left(\frac{k'_{AB}}{M_A} + \frac{K_{AB}}{M_A D_{AB}} \right) \left[\frac{k'_{AA}}{M_A} + \frac{K_{AB}}{D_{AB}} \left(\frac{1}{4M_A} + \frac{2}{M_B} \right) \right]}{3}}$$

If $k_{AB} \ll k_{AA}$ and $k_{AB}/D_{AB} \ll k_{AA}$, then the three slow frequencies, namely, the symmetrical, the twofold degenerate and one threefold degenerate, will be pure vibrations of the A atoms. The ratio of these three frequencies, symmetrical : threefold degenerate : twofold degenerate should then be $1 : \frac{1}{\sqrt{2}} : \frac{1}{2}$.

The Symmetrical-top Molecule BCA_3

As examples of this type of molecule the methyl halides may be mentioned. The molecule has a threefold symmetry around the BC axis.

There are nine vibrational degrees of freedom, of which three are symmetrical vibrations and three are twofold degenerate vibrations. All vibrations may appear both in the infrared spectrum and the Raman effect. The depolarization factor for the degenerate vibration is $3/4$ (or $\approx 6/7$). For the methyl halides the rotational structure is simplified by the fact that the moment of inertia around the halogen-carbon axis is small, and as a first approximation one may consider the rotation to take place around this "fixed" axis.

Since the explicit expressions for the frequencies are rather complicated, only an approximate method will be given. First the BA_3 and the BC groups will be considered separately. The BA_3 group is a symmetrical pyramidal model. Its two symmetrical and two degenerate frequencies are given under that heading. The BC group has a "valence" vibration which is, of course, symmetrical. In addition, the BC group will give rise to a degenerate vibration which is also a deformation one, the BC group, with unchanged BC distance, changing its orientation with regard to the BA_3 group.

The actual frequencies will be approximated by introducing a coupling between the frequencies of the two groups. Of course only vibrations of the same symmetry will disturb each other. If M_B is great compared to the other masses, the coupling of the symmetrical vibrations will be small. With increasing ABA angle the coupling will decrease between the BC

valence vibration and the symmetrical BA_3 valence vibration, but it will increase between the BC valence vibration and the symmetrical BA_3 deformation vibration. The degenerate BC vibration, in which this group changes its orientation in the field of the BA_3 group, will be in general more strongly coupled to the degenerate valence vibration of BA_3 . The general rule that coupling between two frequencies becomes strongly effective only if the difference of the two frequencies is small, and that the coupling tends to increase the frequency differences, also applies here.

The Symmetrical Molecule A_2BC_2

An example of this type of molecule is dichloromethane, H_2CCl_2 . The molecule has two perpendicular planes of symmetry, one passing through the BA_2 atoms and the other passing through the BC_2 atoms. Of the nine vibrations of the molecule, four are symmetrical and five are antisymmetrical. Of the latter, two are antisymmetrical to the BA_2 plane and symmetrical to the BC_2 plane, two are antisymmetrical to the BC_2 plane and symmetrical to the BA_2 plane and one is antisymmetrical to both the BA_2 and the BC_2 planes.

All vibrations may be expected in the Raman effect with the antisymmetrical ones having the depolarization factor $3/4$ or $\approx 6/7$. But in the infrared spectrum only eight frequencies are permitted because the vibration which is antisymmetrical to both planes cannot appear.

Only this brief qualitative discussion of the frequencies will be given here since this molecule can be considered as consisting of the two groups BA_2 and BC_2 . The vibrations of these separate groups have already been discussed. The internal vibrations of BA_2 contribute two symmetrical vibrations and one vibration which is antisymmetrical to the BC_2 plane. The internal BC_2 vibrations give two more symmetrical vibrations, and one which is antisymmetrical to the BA_2 plane. The three remaining antisymmetrical vibrations of the molecule are obtained from changes of orientation of the two groups relative to each other.

To improve the approximation, coupling should be introduced between the different vibrations of the same symmetry. As has been stated repeatedly, this coupling becomes particularly important for the frequencies which are close to each other.

The Ethylene Molecule

This molecule has three planes of symmetry: the plane of the molecule, which will be called the primary plane; a plane passing through the C—C axis and perpendicular to the plane of the molecule, which will be called the secondary plane; and a tertiary plane which is perpendicular to the

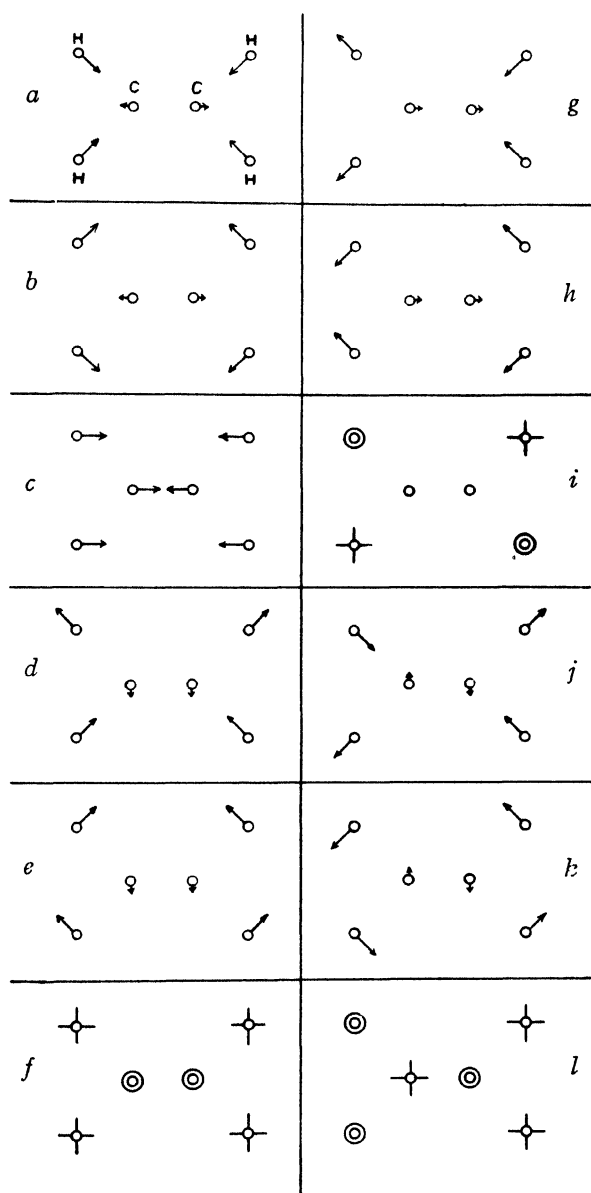


FIGURE 16. The Vibrations of Ethylene. The vibrations *d*, *e*, *f*, *g* and *h* are present in infrared absorption and *a*, *b*, *c*, *d*, *k* and *l* in the Raman Effect, while *i* is absent in both.

C—C axis and passes through the center of symmetry of the molecule, that is, through the center between the two carbon atoms.

The molecule has altogether twelve vibrations illustrated in a qualitative way in Figure 16. Three of them are symmetrical as shown in Figure 16*a,b,c*; two are antisymmetrical only to the secondary plane (Figure 16*d,e*); one is antisymmetrical only to the primary plane (Figure 16*f*); two again are antisymmetrical only to the tertiary plane (Figure 16*g,h*); one is antisymmetrical to all three planes (Figure 16*i*); two are antisymmetrical to the secondary and the tertiary plane (Figure 16*j,k*) and one is antisymmetrical to the primary and tertiary plane (Figure 16*l*).

Since the molecule has a center of symmetry, no vibration can appear both in the Raman effect and in the infrared spectrum. Actually the vibrations of Figure 16*a,b,c,j,k,l* may be expected in the Raman effect. Of these, the ones in Figure 16*j,k,l*, being antisymmetrical, should have a depolarization factor of 3/4 or $\approx 6/7$. In the infrared the vibrations of Figure 16*d,e,f,g,h* should be present. The vibration shown in Figure 16*i*, which is antisymmetrical to all planes, should be present neither in the infrared nor in the Raman effect. One may obtain this frequency from the specific heat or from the overtones and combination tones.

The vibrations *a,c,d,g,j* of Figure 16 may be considered as valence vibrations, the others as deformation vibrations. The frequencies indicated in Figure 16*a,d,g,j*, in which the hydrogen atoms vibrate along their bonds, may be expected to be fairly similar. These similar frequencies may be obtained by considering the vibration of the independent C—H radical. Of course the frequency need not be the same as that of a *free* C—H radical since the force constants in a free C—H radical, and in a C—H radical which is a part of the ethylene molecule, may be different.

In the valence vibration, Figure 16*c*, it is mainly the C—C distance which is changing. Because of the heavier masses involved the frequency will be lower than for the C—H vibrations. The frequency can be obtained in first approximation from the formula $\frac{1}{2\pi} \sqrt{\frac{k}{m}}$, where k is the force constant of the C—C bond and m is the reduced mass of the two vibrating groups, *i. e.*, $m_{\text{H}} + \frac{m_{\text{C}}}{2}$. In the remaining vibrations the frequencies are determined by the force constants of the various angles which change during those vibrations. The frequencies shown in 16*b* and 16*h* will probably be higher than the others. All deformation vibrations in this case are essentially hydrogen vibrations.

It is useful to consider the molecule as consisting of two CH₂-groups. Since the two groups will have exactly the same frequency, the coupling between them will become of importance. Each vibration of a CH₂-group

will give rise to two vibrations of the ethylene molecule. In one, the two CH_2 -groups vibrate in the same phase, in the other they vibrate in the opposite phase. The pairs of vibrations thus obtained are shown in Figures 16a-g, 16b-h and 16d-j. In 16e,f,k,l the CH_2 -groups change their relative orientations. These changes of orientation are again coupled and, as a consequence, they will take place with the same phases and the opposite phases respectively in the pairs 16e-k and 16f-l. It may be expected that the coupling, and therefore the frequency difference, will be greater for these pairs than it was for the pairs 16a-g, 16b-h and 16d-j. It will be noticed that in each of the pairs 16a-g, 16b-h, 16d-j, 16e-k, 16f-l, one vibration appears in the infrared spectrum and in the other occurs the Raman effect.

The Ethane Molecule

The configuration of the atoms in the ethane molecule is not known definitely. It is not impossible that the two CH_3 -groups may rotate around the C—C axis freely and independently of each other. It is to be remembered that in a chemical sense free rotation is of course a well-known fact. This means only that the forces occurring in a chemical reaction are sufficient to rotate the two CH_3 -groups relatively to each other. The important factor is the question whether the thermal energy at room temperature is sufficient to cause rotation. However, it will be assumed that the atoms are bound to definite equilibrium positions, because the designation of normal vibrations is valid only in that case. The probable effects of free rotation will be treated later. The experimental evidence concerning free rotation, or rather the lack of it, is presented in Chapters 7 and 8.

There are two plausible equilibrium configurations. In one, a plane of symmetry passes vertically through the C—C axis so that the two CH_3 -groups are mirror images of each other. The second possible configuration is obtained from the first by rotating one CH_3 -group by 60° around the C—C axis. The two models lead, however, to the same conclusions about the infrared spectrum and the Raman effect, so that it will be sufficient to discuss the first model.

The molecule has eighteen vibrational degrees of freedom. Of these, six are nondegenerate and six are twofold degenerate. Of the nondegenerate vibrations, three are symmetrical, two are antisymmetrical to the plane of symmetry which is perpendicular to the C—C axis, and one is antisymmetrical to both this plane and to planes passing through the axis. Of the degenerate vibrations, three are symmetrical to the plane perpendicular to the C—C axis and three are antisymmetrical to the same plane.

The three symmetrical vibrations may appear in the Raman effect. The same holds for those degenerate vibrations which are antisymmetrical to

the plane perpendicular to the C—C axis. For the latter vibrations the depolarization factor is $3/4$ or $\approx 6/7$. In the infrared the two nondegenerate vibrations may occur antisymmetrical to the plane perpendicular to the C—C axis, as well as the three degenerate vibrations which are symmetrical to the same plane. The nondegenerate vibration which is antisymmetrical to all planes of symmetry does not appear in either the infrared spectrum or the Raman effect. This is the vibration which, if it had a frequency of zero, would become a free rotation of the two methyl groups relative to each other.

The molecule has five valence vibrations: one nondegenerate C—C vibration and four C—H vibrations of which two are degenerate and two nondegenerate. In addition, one of the degenerate and one of the nondegenerate vibrations are symmetrical to the plane perpendicular to the C—C axis. The other two vibrations are antisymmetrical to this plane. Statements similar to those made for ethylene hold approximately for the frequencies of the valence vibration. The remaining vibrations of the molecule are deformation vibrations. They are essentially hydrogen vibrations.

Again the molecule may be considered as consisting of two coupled CH_3 -groups. Each group has two symmetrical and two degenerate vibrations. Since the two groups may vibrate in the same phase and in opposite phases, four symmetrical and four degenerate vibrations are obtained. Of the pairs of vibrations, which differ only in the relative phases of the CH_3 -groups, one should appear in the infrared and the other in the Raman effect. Their frequency difference is due to the coupling of the two groups. A further pair of degenerate vibrations is obtained from the change of orientation of the CH_3 pyramid axis against the C—C axis. This change may happen for the two CH_3 -groups in phase or out of phase, giving rise to an infrared active and a Raman active vibration. The remaining two vibrations are the C—C valence vibration and the relative rotation of the two CH_3 -groups around the molecular axis.

If there is free rotation, only seventeen vibrational degrees of freedom remain, because the vibration which should be antisymmetrical to all symmetry planes appears now as the internal rotation. The degenerate vibrations which could not appear in the infrared spectrum or the Raman spectrum may appear now with small intensities.

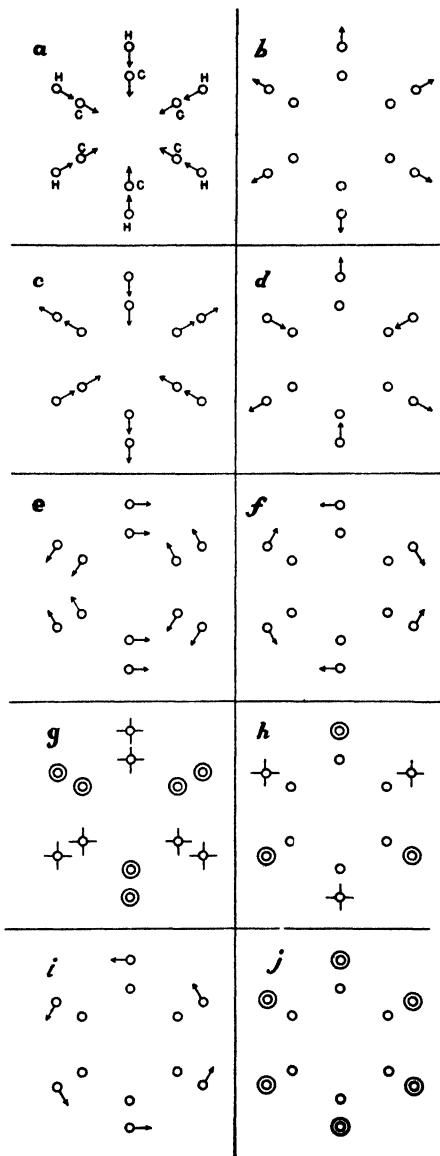
The Benzene Molecule

Benzene has thirty vibrational degrees of freedom of which ten are nondegenerate and ten are twofold degenerate.

Figure 17 shows the nondegenerate vibrations in a qualitative way. Of these *17a* and *17b* are symmetrical and are the only nondegenerate vibrations which may appear in the Raman effect. The other nondegenerate

FIGURE 17.

The Nondegenerate Vibrations of Benzene. The vibrations *a* and *b* are present in the Raman Effect and *j* in infrared absorption. The remainder are absent in both. *In those vibrations which are essentially hydrogen ones, b, d, f, h and i and j, the small displacements of the carbon atoms are not shown by the usual arrows.*



vibrations are antisymmetrical, but they differ in the planes to which they are antisymmetrical. The pairs 17*c,d*, 17*e,f* and 17*g,h* have the same symmetry properties. In Figure 17*j* is shown the only nondegenerate vibration which may appear in the infrared spectrum. In Figures 17*a,c,e,g* the vibrations are essentially carbon vibrations, and the others are hydrogen vibra-

tions. Figures 17*a,b,d,e* represent valence vibrations. The others are deformation vibrations.

The degenerate vibrations are shown qualitatively in Figure 18. The vibrations indicated in 18*a,b,c,d* have the same symmetry properties and are expected to be visible in the Raman effect. Those shown in 18*e,f,g* again have similar symmetry properties and may be present in the infrared spectrum. The type indicated in 18*h,i* form another symmetry class which does

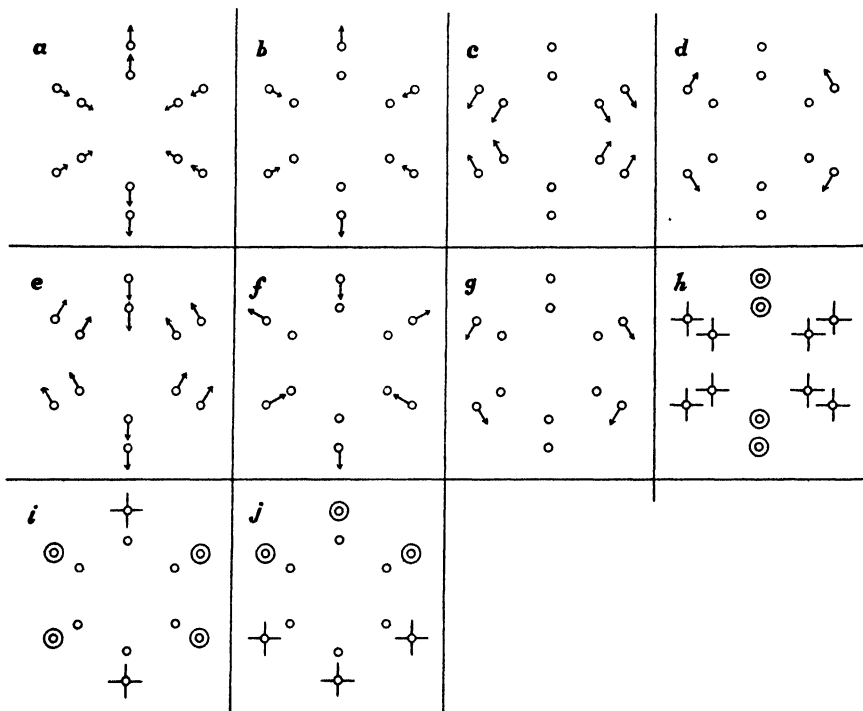


FIGURE 18. The Degenerate Vibrations of Benzene. The vibrations *e*, *f* and *g* are present in infrared absorption and *a*, *b*, *c*, *d*, and *j* in the Raman Effect, while *h* and *i* are absent in both. In those vibrations, which are essentially hydrogen ones, *b*, *d*, *f*, *g*, *i* and *j*, the small displacements of the carbon atoms are not shown by the usual arrows.

not appear either in the infrared or the Raman spectra. On the other hand 18*j* should be present in the Raman spectrum. All degenerate vibrations which appear in the Raman spectrum should have, of course, a depolarization factor of $3/4$ or $\approx 6/7$. The Figures 18*a,c,e,h* represent carbon vibrations and the others are hydrogen vibrations. The vibrations designated as 18*b,c,e,f* may be considered as valence vibrations, while the others are

deformation ones. The four hydrogen valence vibrations, $17b,d$ and $18b,f$ should have similar frequencies.

Complicated Molecules

In more complicated molecules the symmetry has less importance than in the examples hitherto discussed. Often the molecule has no symmetry whatever and all vibrations should be considered then as "symmetrical." All of them may appear in both Raman and infrared spectra. No strict degeneracy exists.

In attempting to ascertain the frequencies in a qualitative way it is useful to consider the valence and deformation vibrations separately. The former have the higher frequencies. It is also an advantage to make distinctions according to the kinds of atoms which participate in the vibration. The heavier the vibrating atoms are, the smaller the frequency will be. But a hydrogen deformation vibration may have the same frequency as a carbon valence vibration, and coupling between these two may bring about vibrations which may not be properly called either hydrogen or carbon valence or deformation vibrations.

It may further simplify the problem to consider the smaller groups within the complicated molecule, to calculate the frequencies for each of them, and then to take into account the coupling. It is to be borne in mind, as has been stated previously, that the coupling of vibrations which takes place at a distance is generally small.

If hydrogen atoms are attached to a heavier atom such as carbon, nitrogen or oxygen the whole CH_2 , CH_3 , NH_2 , NH or OH group may at first be considered as one atom. It may become necessary to modify the results thus obtained on account of the hydrogen deformation vibrations; but the hydrogen valence vibrations can always be treated separately from all other vibrations inasmuch as they have much higher frequencies.

A particularly simple case presents itself if we have long-chain molecules consisting of similar groups such as CH_2 -groups. The several groups will then vibrate in the same manner but with varying amplitudes if not perturbed by other groups or atoms not belonging to the simple chain. Should the groups be numbered and the amplitude in a group plotted against its number, an approximate sine curve would be obtained, if an opposite phase is taken as a negative amplitude.

It will be of interest to see what happens if the groups of the chain are considered as atoms which will be designated by A, this procedure being to a certain extent justified by the reasons given above. In this treatment only the valence vibrations will be considered. If the chain is straight its frequencies will range from nearly zero, corresponding to a compression

and expansion of the whole chain, to a maximum of $\frac{1}{2\pi}\sqrt{\frac{4k_{AA}}{M_A}}$, corresponding to a motion in which neighboring atoms have the same amplitude but opposite phase. If, on the other hand, the chain is not straight and if the AAA angle is denoted by α , the frequencies will range from $\frac{1}{2\pi}\sqrt{\frac{2k_{AA}(1-|\cos \alpha|)}{M_A}}$ to $\frac{1}{2\pi}\sqrt{\frac{2k_{AA}(1+|\cos \alpha|)}{M_A}}$. For a paraffin chain with $|\cos \alpha| = 1/3$ this gives a rather limited range of frequencies. Among these frequencies the lowest will probably have the strongest Raman line since in this vibration all bonds contract and expand simultaneously.

If a group such as a chlorine atom or a nitro- group is attached to the chain and if a frequency of this group falls within the range of the vibrations of the chain, then the vibration of the group will become indistinguishably intermingled with the vibrations of the chain. It then becomes meaningless to say which frequency belongs to the group vibration and which to the chain vibration. The chain vibration will be, of course, perturbed and the rule about the Raman intensity will not hold.

If, however, the group vibration lies outside the range of the chain vibrations, then both will be only slightly modified. This is true, for instance, in the case of the C—Cl vibration, which is lower than the lower limit of the vibrations of a hydrocarbon chain. The C—F vibration, on the other hand, becomes blended with the C—C vibrations.

Even if the frequency of a group vibration is not strongly influenced by the chain vibrations, it is not necessarily true that the vibration is localized in the group in question in a definite manner. It can be shown that if a group vibration lies outside the range of the chain vibrations, then the subsequent members of the chain will participate in the vibration with amplitudes which decrease exponentially as one proceeds along the chain away from the group. Thus even though there may be an influence of the chain on the group vibration, this influence is the same for all chains of the same kind, provided the chains are not too short.

Chapter 6

Factors Which May Modify Vibrational and Rotational Raman Spectra

The Isotope Effect

Even after the frequencies of a polyatomic molecule are determined, one is still far from having a detailed knowledge of the elastic forces. This knowledge is available only if both the frequencies and the forms of the vibrations are known. Some help in this respect is obtained from assumptions such as the valence force or central force models, but they can give at best only approximate results.

The difficulty can be put in a more exact form by remembering that the frequencies are roots of the equation

$$(95) \quad \begin{vmatrix} a_{11} + m_1 4 \pi^2 \nu^2 & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} + m_2 4 \pi^2 \nu^2 & \dots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} + m_n 4 \pi^2 \nu^2 \end{vmatrix} = 0$$

If the roots of this equation, *i. e.*, the n frequencies, are known, there is available independent information about the force constants a_{ik} . But even taking into account the relation $a_{ik} = a_{ki}$ there are $\frac{n(n+1)}{2}$ force constants a_{ik} to be calculated.

The situation becomes somewhat more hopeful if the symmetry of the molecule is taken into account, since the symmetry will cause certain force constants to become equal or related to each other and will thus reduce the number of unknowns. At the same time, however, by causing degeneracies it may also reduce the number of different molecular frequencies, that is, the number of independent sources of available data.

The situation brought about by the symmetry may be visualized as follows. There will be groups of vibrations with the same symmetry. The vibrations in any one group are independent of the other vibrations of the molecule and may be treated independently. If there are f vibrations in one symmetry group, the f frequencies will be solutions of a determinant equation such as (95), but with only f rows and columns. Thus there will

be f known data but $\frac{f(f+1)}{2}$ unknown force constants for this symmetry class.

If the symmetrical nonlinear molecule BA_2 is taken as an example there are two symmetrical and one antisymmetrical vibrations. For the antisymmetrical vibration we have $f = 1$ and $\frac{f(f+1)}{2} = 1$. Thus, by knowing the frequency we know all about this type of vibration. It has been emphasized several times that if a vibration is the only one of its symmetry type, its form of vibration is determined by the symmetry and by the form of the molecule, and the frequency of this vibration is the only thing about it that remains to be determined.

For the symmetrical vibrations, however, there are $f = 2$ frequencies, but $\frac{f(f+1)}{2} = 3$ force constants, and in this case not all force constants can be obtained from knowledge of the two frequencies.

Among the methods of obtaining a more complete knowledge of the force constants, the most effective is to substitute isotopes for some of the atoms of the molecule, and to observe the way in which the frequencies are shifted. An isotopic substitution does not change either the form of the molecule or the force constants. Thus the unknown constants are not increased. It does change the frequencies, and thus the number of available data are increased.

To this a further advantage must be added. By substituting isotopes for some of the atoms in symmetrical positions, for example by substituting deuterium atoms for some of the hydrogen atoms in benzene, the symmetry of the molecule may be effectively reduced. Since isotopes in symmetrical positions will vibrate differently from the atoms which they replaced, some frequencies which, because of the symmetry, were not present in the Raman or infrared spectra may appear as a result of the substitution. This is particularly desirable in molecules such as benzene in which, because of the symmetry, a great number of vibrations do not appear either in the Raman or in the infrared spectra. If care is taken to insert isotopes only in certain positions, such as the 1,3,5-positions in benzene, a complete analysis can be obtained on this basis.

This complete analysis is, of course, rather complicated and will not be carried out here (see Chapter 15). But a simpler rule will be mentioned which is of help in deciding to which symmetry type a certain observed frequency belongs.

According to the theory of determinants and to equation (95) the product of the square of all molecular frequencies satisfies the relation

$$(96) \quad \pi_i (4\pi^2 \nu_i^2) = \frac{1}{\pi_i \bar{M}_i} \cdot \begin{vmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{vmatrix}$$

where the sign π_i means that the product is taken of all the quantities having the different subscripts i . In this product of frequencies, the frequencies of the translational and rotational vibrations must be included. It will be remembered that such translational and rotational vibrations were brought about by artificial forces which were introduced in order to give the molecule a definite equilibrium position and equilibrium orientation in space. The magnitude of these artificial forces is immaterial in the following argument and they may, therefore, be permitted to approach zero without invalidating the results.

If now the product of the frequencies of the original molecule is divided by the product of the frequencies which are obtained after isotopic substitution, there is obtained:*

$$(97) \quad \frac{\pi_i \nu_i^2}{\pi_i \bar{\nu}_i^2} = \frac{\pi_i \bar{M}_i}{\pi_i \bar{M}_i}$$

In this expression, $\bar{\nu}_i$ are the frequencies and $\bar{M}_i$ the masses after isotopic substitution; the determinant on the right hand side of (96) has disappeared because the force constants, and therefore also the determinant, remain unchanged if the isotopes are introduced.

The product rule in its present form is still of little use since it includes the translational and rotational vibrations. It is not difficult, however, to eliminate these, inasmuch as the isotopic substitution will change the square of a translational frequency by the inverse ratio of the molecular masses before and after the substitution, and it will change the square of a rotational frequency by the inverse ratio of the corresponding moments of inertia.

Thus if deuterium atoms are substituted for all the hydrogen atoms in benzene and the product is taken over the proper frequencies (leaving out the translational and rotational frequencies), there is obtained:

$$(98) \quad \frac{\pi_i \nu_i^2}{\pi_i \bar{\nu}_i^2} = 2^{18} \left(\frac{78}{84} \right)^3 \left(\frac{M_C D_C^2 + M_H D_H^2}{M_C D_C^2 + 2M_H D_H^2} \right)^3$$

* A twofold degenerate frequency must be introduced in the frequency products (96) and (97) just as though two separate vibrations of the same frequency were present. A threefold degenerate vibration corresponds to three distinct vibrations of the same frequency.

The masses of the carbon atoms remain the same; consequently their ratio is $\frac{\overline{M}}{M} = 1$. For the hydrogen atoms, however, the mass ratio becomes $\frac{\overline{M}}{M} = 2$. As each hydrogen atom may move in the x, y, z directions, and as a different index has been attached to the mass of the same atom in connection with every separate direction in which the atom can move, each deuterium substitution gives a factor 2^3 . The six substitutions therefore give 2^{18} . The ratio of the molecular masses is $\frac{84}{78}$ and the factor $\left(\frac{78}{84}\right)^3$ has been introduced to compensate for the three translational vibrations.

Similarly $\frac{M_C D_C^2 + 2M_H D_H^2}{M_C D_C^2 + M_H D_H^2}$ is the ratio of the moments of inertia and

$\left(\frac{M_C D_C^3 + M_H D_H^3}{M_C D_C^2 + 2M_H D_H^2}\right)^3$ compensates for the rotational vibrations, where D_C and D_H are the distances of the carbon and hydrogen atoms from the center of the molecule.

The product rule can be made more useful by applying it to each symmetry class of vibrations separately. It has been mentioned above that the frequencies of vibrations of the same symmetry may be obtained from a determinant equation similar to (95) but involving fewer rows and columns. Accordingly a product rule may be obtained with the help of considerations similar to those which have been described for the molecule as a whole. The ratio of the square products of the frequencies will now be given by the mass ratio of the isotopes raised to the number of vibrations which the atom in question contributes to the vibrations of the particular symmetry type. If a translational or rotational vibration has the same symmetry as the vibrations under consideration, then a correction must be introduced in the form of a ratio of molecular masses or of moments of inertia.

These conditions will become clearer by applying them to the ratio of frequencies of benzene, C_6H_6 and benzene- d_6 , C_6D_6 . To the symmetrical vibrations shown in Figures 17*a* and *b* the hydrogens contribute one vibration. No translational or rotational vibration has the same symmetry as these vibrations. Therefore the ratio of the squares of the frequency products for the symmetrical vibrations is $\frac{M_D}{M_H} = 2$. The same holds for the two vibrations 17*c,d*, for 17*e,f*, and for 17*g,h*. The vibration 17*i* is the only one of its symmetry type, but the rotation about an axis perpendicular to the molecular plane belongs to the same symmetry type. The hydrogen atoms contribute one vibration to this type. Thus the

square of the frequency $17i$ for benzene, divided by the square of the same frequency for benzene- d_6 , is $2 \left[\frac{M_C D_C^2 + M_H D_H^2}{M_C D_C^2 + 2M_H D_H^2} \right]$.

The vibration $17j$ is again the only one of its symmetry, and once more the hydrogen atoms contribute one vibration. A translation perpendicular to the molecular plane has the same symmetry. Thus the ratio of the square frequencies for $17j$, for benzene and benzene- d_6 , is $2 \left(\frac{78}{84} \right) = \frac{13}{7}$. To the degenerate vibrations $18a, b, c, d$ the hydrogen atoms contribute two vibrations. No rotation or translation has the same symmetry. Therefore the square product ratio will be $\frac{M_D^2}{M_H} = 4$. To the vibrations $18e, f, g$ two vibrations are contributed to the hydrogen atoms. A translation in the molecular plane has the same symmetry. The square product ratio will be $4 \left(\frac{78}{84} \right) = \frac{26}{7}$. To the type indicated by $18h, i$ the hydrogen atoms contribute one vibration. No translation or rotation has the same symmetry. The square product ratio is 2. To the type of $18j$ the hydrogen atoms again contribute one vibration. A rotation around an axis in the molecular plane has the same symmetry. The square frequency ratio is, therefore,

$$2 \left[\frac{M_C D_C^2 + M_H D_H^2}{M_C D_C^2 + 2M_H D_H^2} \right]$$

As has been mentioned, a partial isotopic substitution may effectively destroy some symmetry properties of the molecule. If, for instance, only one deuterium atom is substituted in benzene, all symmetries are reduced to two planes of symmetry, namely, the plane of the molecule and a plane perpendicular to it and passing through the C—D bond. In this case the detailed product rules can be applied only to the greater group of frequencies which have the same symmetry properties with regard to the symmetries *not* destroyed by the substitution. In the example given above a product rule will hold for the frequencies symmetrical to both remaining planes. These frequencies will include, for instance, those shown in Figures $17c, d$ for benzene, which have not been called symmetrical. Another will hold for the vibrations antisymmetrical to the molecular plane but symmetrical to the second plane; a third will hold for those antisymmetrical to the second but symmetrical to the molecular plane; and a fourth will hold for the vibrations antisymmetrical to both planes. Thus much fewer product rules are obtained than for benzene- d_6 in which the molecular symmetry remains complete.

It must also be mentioned that degenerate vibrations may split into two or more nondegenerate vibrations if the symmetry of the molecule is sufficiently reduced. This will be the case in the example of benzene-d₆ given above.

Except for the hydrogen isotopes the difference of the isotopic masses $\overline{M} - M = \Delta M$ is always small compared to the mass, M , of the atom. In this case the frequency shift, $\overline{\nu} - \nu = \Delta\nu$, will be small compared to ν and the product rule can be written in a simpler form. This is done by replacing in (97) $\frac{\pi_i \nu_i^2}{\pi_i \overline{\nu}_i^2}$ by $-\sum_i \frac{\Delta\nu_i}{\nu_i}$ and $\frac{\pi_i \overline{M}_i}{\pi_i M_i}$ by $\sum_i \frac{\Delta M_i}{M_i}$. The ratios of the molecular masses and of the moments of inertia must be substituted similarly by the sums over the relative changes of these quantities. If one kind of isotope has been substituted, the sum rule which has been obtained in this way may be stated by setting

$$(99) \quad \frac{\Delta\nu_i}{\nu_i} = -1/2 \frac{\Delta M_i}{M_i} \zeta_i,$$

where ζ_i is a pure number characteristic for the vibration. The sum rule specifies that the ζ_i values summed over all vibrations of a certain symmetry type give the number of vibrations which the substituted atoms contribute to the vibrations of that symmetry.

It can be shown that the number ζ_i has a simple physical significance. It gives the ratio of the sum of the kinetic energies of the substituted atoms to the sum of the kinetic energies of all atoms, for the vibration which is considered. Thus the isotopic substitution (with $\Delta M \ll M$) gives direct information about the question of how strongly an atom participates in a certain vibration.

Effect of the Anharmonicity

As has been mentioned already, the most important effect of the anharmonicity is that it causes the appearance of overtones and combination tones. A second effect, caused by the mechanical anharmonicity alone, is that the frequency of the vibration changes with the amplitude. In diatomic molecules the frequency will, as a rule, decrease with increasing amplitude. For polyatomic molecules this rule cannot be expected to hold in general, although there are not many examples to the contrary. Moreover for polyatomic molecules the frequency of one vibration may be influenced by the amplitude of another vibration.

The dependence of the frequencies on the amplitudes, according to classic theory, will cause a broadening which increases with temperature. This is because the atoms in molecules will vibrate with all kinds of amplitudes and therefore with a certain range of frequencies.

In the quantum theory the consequence of the anharmonicity becomes somewhat more complicated. If there is no mechanical anharmonicity the energy levels of the oscillator are spaced at equal distances $h\nu$, where ν is the frequency of the oscillator. Transitions between two neighboring levels will correspond to absorption or emission of the oscillation frequency. The fact that the frequency changes with the amplitude from the classic standpoint has its corresponding counterpart in the quantum theory. The energy difference between two higher neighboring levels will no longer be the same as that of two lower neighboring levels. As a result, several finely spaced lines may be obtained instead of one vibrational line when the temperature is high enough to excite higher levels. This structure takes the place of the classic continuum. It is usually blurred by the rotation structure. Furthermore, if the temperature is too low, so that the oscillator does not contribute to the specific heat ($kT \ll h\nu$), only the first line of the structure will have any appreciable intensity.

The quantum explanation of the appearance of overtones is that transitions may occur between other than neighboring levels. The phenomenon likewise differs to some extent in the classic and quantum theories. In classic theory the first overtone has strictly twice the frequency of the fundamental. In quantum theory, as soon as mechanical anharmonicity is present and the vibrational levels are not spaced quite uniformly, the 0—2 transition, corresponding to the first overtone, will not have exactly twice the frequency of the 0—1 transition, corresponding to the fundamental tone. In a similar way, in classic theory a combination tone is exactly the sum or difference of two simpler frequencies, whereas in quantum theory this rule holds only approximately.

Of greater practical importance than these small effects is the case of an overtone or a combination tone getting into resonance with a fundamental tone. This is frequently termed the Fermi resonance effect. An example is furnished by carbon dioxide, where the frequency of the degenerate vibration is one-half that of the symmetrical vibration (cf. Figures 8 and 10). Now in the time interval consumed by two passages of the carbon atom between the two oxygen atoms in the degenerate vibration, half a period of the degenerate vibration elapses. This happens to be equal to the period of the symmetrical vibration. The oxygen atoms thus may be pulled together and pushed apart, through the effect of anharmonicity, every time the carbon atom just passes between them or is in a position as far away as possible from the 0—0 line. Thus a resonance with the symmetrical vibration is established.

The quantum representation of this same situation is as follows. The second excited level of the degenerate vibration happens to coincide with the first excited level of the symmetrical vibration. Now the anharmonicity

may establish a coupling between these two levels, although such a coupling may be prohibited by reasons of symmetry, in which case this effect will not occur. For carbon dioxide the symmetry permits such a coupling. The effect is similar to that of the coupling between molecular vibrations. Instead of the two coinciding levels there will be two levels of somewhat different energies, of which neither can be called "the second level of the degenerate vibration" or "the first level of the symmetrical vibration"; but both levels contain something of the properties of the two original levels.

Now the transition from the fundamental level of the molecule to the first excited level of the symmetrical vibration should take place in the Raman effect with the strong intensity of a fundamental, while on the other hand the transition to the second level of the degenerate vibration will have the small intensity of an overtone. Both levels resulting from the coupling will contain some of the properties of the first excited level of the symmetrical vibration. Therefore transitions to both levels will have part of the properties of the transition to the first excited state of the symmetrical vibration and will have intensities comparable to a fundamental tone. Actually the intensity of the fundamental tone of the symmetrical vibration will be shared between the two lines and the resulting spectrum will contain an additional strong line. The same situation may also occur if a combination tone and a fundamental tone resonate.

Influence of the Resonance Fluorescence

The polarizability theory of the Raman effect is valid only as long as the irradiated frequency is sufficiently far away from any absorption frequency of the molecule. The difference between the exciting frequency and any absorption frequency must be great as compared to the frequencies of molecular vibration.

If the absorption frequency is used as the exciting frequency the resonance fluorescence spectrum, which is much more complicated than the Raman spectrum, will be obtained. Instead of just the fundamental tones and a few weak overtones, whole series of the same frequency may appear with appreciable intensities in fluorescence. Moreover, even the vibrational frequencies of the molecule in the excited state may appear; and, since these may differ from the frequencies in the fundamental state, the spectrum will be still more complicated.

But even at some distance from the absorption frequency an incipient effect of the resonance fluorescence may appear and cause deviations from the simple polarizability theory. The first effect is that the polarizability of the molecule will depend not only on the configuration of the nuclei but also on their velocity. This will cause changes of intensity and also the appearance of frequencies in the Raman effect which, according to the

polarizability theory, would be prohibited by the symmetry. Moreover the statements for the polarizability $\alpha_{xy} = \alpha_{yx}$, $\alpha_{yz} = \alpha_{zy}$, $\alpha_{zx} = \alpha_{xz}$ can be derived only from a *static* model of the atom; and as soon as the velocities of the atoms become important these equalities no longer hold. As a consequence of this, the polarization of the scattered radiation may become anomalous. It may even happen that, if polarized light is used as the exciting radiation, light polarized at right angles to the original direction of polarization is scattered.*

Therefore, although the intensity of the Raman lines increases very strongly if an absorption line is approached, the investigations have to be carried out using a source of radiation whose exciting wave-length does not lie too close to any absorption band. Otherwise the simple theory of the Raman effect is not applicable and no simple conclusions can be drawn from the experimental results.

Influence of the Solid and Liquid States

The coupling of molecules in a crystal lattice will make it necessary, in principle, to consider the whole lattice as one big molecule. The normal vibrations of this supermolecule are, however, not too difficult to find.

To each vibration of a single molecule there will correspond a series of vibrations of the lattice in which each molecule vibrates virtually as if it were alone. But other molecules of the same kind vibrate with different amplitudes, giving rise to a picture similar to that which has been obtained for the long-chain molecule. The fundamental tone of only those vibrations in which all molecules oscillate with the same phase and amplitude can appear in both the infrared and Raman spectra, since otherwise the effects of the different molecules would destroy each other through interference. The phases referred to above must not be the same in the whole crystal, but only in a region comparable to the wave-length of light. This distinction has, however, only small practical significance, inasmuch as only one optically observable vibration of the crystal will correspond to each molecular vibration. Thus the observed frequencies in the solid remain sharp and are only slightly shifted from the normal positions observed for the isolated molecule in the gaseous state. Because rotation in the solid state is possible but frequently absent, the missing rotational structure may make the lines sharper than in the gas. Crystal vibrations, however, may cause some broadening of the lines. Overtones and combination tones may appear in crystal vibrations, while the molecules may be vibrating with differing amplitudes. This results in a more complicated and broadened

* Such anomalous polarization might also occur far from the absorption line if the electrons in the fundamental state of the molecule have angular momentum. This is, however, very rarely the case.

structure for these vibrations. All vibrations in liquids may be expected to be broadened more strongly than in solids.

Apart from the proper intramolecular vibrations, further vibrations may appear in liquids and solids, which are caused by the vibration of the molecules as a whole with respect to one another. Such vibrations may consist either in changes of position or in changes of orientation. These are generally slower than the intramolecular vibrations but, in the lattices which are not proper molecular lattices, they may become indistinguishable from proper molecular frequencies.

If, in a crystal or in a liquid, a symmetrical molecule is in a less symmetrical or in an unsymmetrical surrounding, frequencies may appear which, owing to the symmetry considerations, could not appear in the gaseous state either as infrared or Raman lines. Their intensities will be, however, weak. Even when the surroundings induce a change of dipole moment, or polarizability, which amounts to as much as $1/10$ of the usual dipole or polarizability-change during a vibration, the intensity will be only $1/100$ of the intensity of a normal fundamental vibration. The reason for this is that the intensities are proportional to the squares of the dipole moment (or polarizability) change. This fact, however, makes it possible for intensities which are already great in the gaseous state to be influenced to a considerable degree by the solid or liquid state. Thus if the change of polarizability or dipole moment during a vibration is called 1 in the gas, and if it is modified by $1/10$ in the condensed state, the intensity for the molecule will be changed by the factor 1.2.

No attempt has been made in the last four chapters to acknowledge individually the contributions of many writers to the theoretical aspects of the Raman effect and the vibrations and rotations of polyatomic molecules. This is partly because the views expressed in these chapters represent, on the whole, a consensus of opinion, and partly because the authors who have made these contributions are indicated separately in the Bibliography.

Part II

The Raman Spectra of Organic Compounds

Chapter 7

Saturated Aliphatic Hydrocarbons

The method of presentation in Part II and Part III emphasizes the applications of the Raman effect to constitutional problems. Nevertheless, the theoretical relations of this effect to the vibrational and rotational spectra of simple as well as complicated molecules, when symmetry conditions permit, are not neglected, but will be treated in much less detail than is given in Chapters 3 to 7. Those who are interested in any of the multitudinous applications of the Raman effect to organic and inorganic chemistry and to biochemistry may therefore ascertain its uses and limitations independently of a detailed and exact presentation of the theory involved. Any attempt at a complete listing of these applications—which include such diverse topics as the constituents obtained by fractional distillation of the naturally occurring terpenes, the constitution of cuprous ammonium complexes, of sulfuric acid and of the complex hydrocarbons and their derivatives—would be premature at this point. On the other hand, the interrelations between the observed results and their empirical interpretation require some knowledge of the theoretical background necessary to produce these results. This is generally given as each individual type of compound is considered. The basic concepts necessary as a prerequisite to the application of the Raman effect in any instance are given in simplified form in the text up to Chapter 3.

It has been already indicated that the magnitude of a Raman shift is a function of the forces existing between the atoms in a molecule, the types of motion of the atoms, the symmetry of the molecule, and the relative masses of the atoms. Organic compounds are particularly illustrative of these relationships—first, because their linkages are almost always homopolar, and secondly, because the type of binding in many cases has been established by chemical means. As the masses of vibrational components decrease, the Raman shifts will increase roughly according to the mass and frequency relations in the equation for a harmonic oscillator. It is not surprising therefore that the shifts corresponding to the linear (ν_r) oscillations of the C—H linkage are of large magnitude. This is exceeded only by the H—H, N—H and O—H linkages. The actual wave number value for the C—H binding will vary from $\Delta\bar{\nu}$ 2850 to 3300, depending on the nature of the compound containing this group.

Such variations are, at least in part, a reflection of a change in the force constant as well as a function of constitution. For the sake of illustration, the calculated force constants and typical wave number shifts corresponding to the linear oscillation of the atoms in groups or in molecules commonly encountered in organic and inorganic chemistry were given in Table 1, page 22.

This illustrates the early derivation of Andrews that the magnitude of the force constant is almost directly proportional to the number of bonds, or shared pairs of electrons, increasing in steps very roughly corresponding to 5×10^5 dynes per centimeter for each bond. For compounds such as halogen acids, whose homopolarity is less marked, the force constant is markedly diminished. When there is complete ionization, such as exists in sodium chloride crystals or in aqueous solutions of hydrochloric acid, the force constant diminishes to zero and no Raman line is obtainable.

Methane

The simplest of the saturated aliphatic hydrocarbons is methane, a molecule of the type AX_4 . Of the nine possible frequencies describing the atomic motions, four should appear in the Raman spectrum but only three are realized. This molecule is a tetrahedron and has a high degree of symmetry (T_d). Of these four possible frequencies, two correspond to triply degenerate asymmetrical vibrations, one is doubly degenerate and symmetrical, and one is nondegenerate and symmetrical. The exact assignment of these observed frequencies can be determined at least partially from their degree of polarization. In general the symmetrical oscillation will be polarized and ρ , the depolarization factor, will be small (*i. e.*, usually varying from 0.03 to 0.25). The doubly degenerate symmetrical oscillation in methane will probably be partially polarized and the remaining asymmetrical ones depolarized ($\rho \approx 6/7$).

The strongest line appearing in methane is at $\Delta\tilde{\nu}$ 2914(10) (ν_1). Two other weak lines $\Delta\tilde{\nu}$ 3022(2) (ν_3) and 3071(1) ($2\nu_2$) are present. The first of these appears also in infrared absorption along with $\Delta\tilde{\nu}$ 1304 (ν_3) and possibly 1520 (ν_2) and 4217, which are absent in Raman spectra. It may be assumed that the two frequencies occurring in infrared absorption may be attributed to the asymmetrical motion of the hydrogen atom, as such absorption can occur only as a result of a change in moment. On the other hand $\Delta\tilde{\nu}$ 2914 is the inactive oscillation, forbidden in infrared absorption, but strong in Raman spectra; consequently it probably arises from the symmetrical motion of hydrogen atoms in the expansion and contraction of the tetrahedron. In liquid methane Daure⁴⁶⁶ and McLennan, Smith and Wilhelm¹⁰⁵³ have observed additional lines.

The order of the shifts from lowest to highest observed in the infrared

absorption and the Raman spectra of methane corresponds to $\nu_4(\text{D})$ ③, $\nu_2(\text{D})$ ②, $\nu_1(\text{P})$, and $\nu_3(\text{D})$ ③, where the depolarization is indicated in parentheses and the degree of degeneracy in circles. With most compounds of the type AB_4 the order is ν_2 , ν_4 , ν_1 and ν_3 (note Table 2).

Deuterium Derivatives of Methane

The results obtained with the deuterium-substituted methanes are indicated in Table 3 which is taken from the work of MacWood and Urey¹⁰⁰⁶. The calculated values given by Dennison and Johnston are shown in parentheses.

Table 3.—Vibrational Raman Frequencies of the Methanes.

CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
ν_1 (2914.2)	ν_1 unobs. (2944)	ν_1 2139.0 (2141)	ν_1 2141.1 (2101)	ν_1 2084.7 (2061)
ν_2 (unobs.)	ν_2 unobs. (1460)	ν_{2a} 1332.9 (1317) ν_{2b} unobs. (1424)	ν_2 1299.2 (1286)	ν_2 unobs. (1075)
$2\nu_2$ (3071.5)	$2\nu_2$ 2921.7	$2\nu_{2b}$ 2916.4	$2\nu_2$ 2512.4	$2\nu_2$ 2108.1
ν_3 (3022.1)	ν_{3c} 2199.5 (2183) ν_{3ab} unobs. (3013)	ν_{3c} unobs. (2227) ν_{3a} 2974.2 (2969) ν_{3b} unobs. (3013)	ν_{3c} unobs. (2992) ν_{3ab} 2268.6 (2222)	ν_3 2258.0 (2227)
ν_4 (unobs.)	ν_{4ab} 1330.1 (1300) $2\nu_{4ab}$ unobs. ν_{4c} unobs. (1151) $2\nu_{4c}$ 2314.8	ν_{4a} 1285.6 (1228) ν_{4b} 1033.1 (1019) ν_{4c} unobs. (1082) $2\nu_{4c}$ 2179.6	ν_{4ab} unobs. (994) $2\nu_{4ab}$ 1963.4 ν_{4c} unobs. (1020) $2\nu_{4c}$ 2092.8	ν_4 unobs. (987)

CH_3D and CHD_3 have a threefold axis of symmetry and therefore will have three nondegenerate parallel vibrations indicated as ν_1 , ν_{3c} and ν_{4c} , and three doubly degenerate perpendicular vibrations such as ν_2 , ν_{3ab} and ν_{4ab} . The molecule CH_2D_2 has a twofold axis of symmetry and consequently all nine possible vibrations are nondegenerate. These are indicated as ν_1 , ν_{2a} , ν_{2b} , ν_{3c} , ν_{3a} , ν_{3b} , ν_{4a} , ν_{4b} and ν_{4c} .

It will be observed that a number of the possible frequencies are missing and some of those present represent combination frequencies. Molecules having the general formulas RX_4 , RX_3Y and RX_2Y_2 and having the symmetry T_d , C_{3v} and C_{2v} should have four, six and nine Raman frequencies respectively, although retaining the tetrahedral spatial arrangement. Of the six frequencies for C_{3v} , three are polarized and three have a value of $\rho \approx 6/7$. Of the nine frequencies for RX_2Y_2 , symmetry C_{2v} , three are

polarized and possibly five have a value of $\rho \approx 6/7$. All these vibrations supposedly are active in Raman spectra.

The actual experimental appearance of Raman lines which are not forbidden is determined by their intensities. In general, overtones and combination tones are considerably weaker than fundamentals, but in special cases this may not follow. In the case of resonance between certain energy states of the molecule due to accidental degeneracy (Fermi resonance), the distribution of the intensity in the frequencies corresponding to these levels is a function of the separation of the levels, the frequency of their vibration, and their anharmonicity. The anharmonicity will increase or decrease the intensity of overtones and combination tones depending on the type of perturbation. Briefly, therefore, the appearance of the Raman lines depends on the symmetry of the molecule, the effect of the atomic motions on the change in polarizability, resonance interaction and the anharmonicity of the vibrations involved. For these reasons the spectrum of the deuteriomethanes shows both the absence of some fundamentals and the presence of overtones.

While one strong line is characteristic of the linear $C \leftrightarrow H$ oscillation or the vibration in the direction of the valence bond in methane, two strong lines, $\Delta\bar{\nu}$ 2900 and 2955, appear in ethane. This multiplicity of hydrogen lines increases with the complexity of the molecules up to butane, after which there is no marked change. The appearance of these new lines is attributed to the perturbing influence of valence forces and to the Fermi

Table 4.—The Hydrogen-to-Carbon Oscillations of Some Simple Hydrocarbons.*

Hydrocarbon	Hydrogen Oscillations in $\Delta\bar{\nu}$								
Methane						2918 (10)		3018 (2b)	3066 (1)
Ethane						2913 (9)	2943 (10)		
Propane	1453 (4)	2728 (3)	2767 (1)	2874 (10)	2903 (3)	2920 (5)	2948 (3)	2968 (3)	
Butane	1453 (10b)	2665 (1)	2706 (1)	2736 (2)	2864 (4)	2879 (8)	2910 (3)	2938 (6)	2964 (3)
Isobutane	1453 (10b)	2624 (1)	2720 (4)	2777 (2)	2870 (10)	2892 (2)	2910 (3)	2936 (3)	2962 (8)

*Values in parentheses indicated relative intensities on a scale of 0 to 10. The letter b indicates a broad line

resonance effect. The valence vibration of the hydrogen atoms attached to the central carbon atom in propane obviously is going to be affected by the adjacent methyl groups. The hydrogen oscillations in ethane and similarly the hydrogen atoms in propane, therefore, are not precisely identical with those in methane. With the lengthening chain new lines

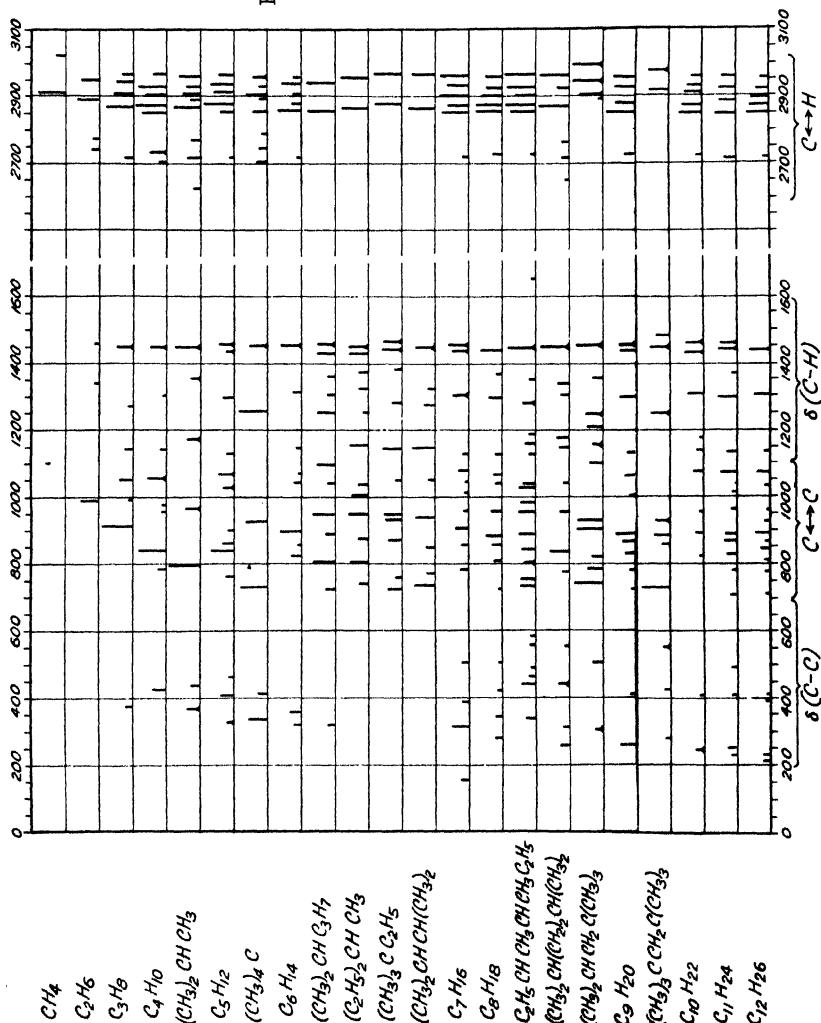
appear at lower frequencies which presumably indicate either a slight loosening of the bond in these compounds, or other types of oscillation not described by the simple T_d or other symmetry considerations. In Table 4 are given the observed hydrogen lines for the hydrocarbons from methane to isobutane. This includes the shift at $\Delta\bar{\nu}$ 1453, which owes its origin to the bending moment of the hydrogen, and is more or less in the direction perpendicular to the linear oscillation. This is a deformation (δ_r) type of vibration, the force constant of which is approximately one-fifth that of the linear type. In the isomeric compounds this either increases in intensity or shows a tendency to become a doublet—that is, is split into two components.

Attempts have been made by Petrikaln,¹²²⁰ Andrews,⁵³ Dadiou and Kohlrausch,⁴³³ High⁷⁴³ and others to assign specific frequencies between $\Delta\bar{\nu}$ 2665 and 2968 to various specific groups, such as the methyl group or a methyl group attached to a sequence of methylene, CH_2 , groups. These have not been entirely successful. The strongest lines occur near $\Delta\bar{\nu}$ 2870 and 2930 in the simpler straight-chain hydrocarbons. In the isomeric derivatives containing a large number of methyl groups $\Delta\bar{\nu}$ 2970 becomes stronger.

It may be mentioned in this connection that each methyl group may be represented roughly as a pyramid having, therefore, two vibrations resulting from a change in electric moment parallel to the figure axis of the group, and two vibrations from a change perpendicular to the axis. It can be seen from Table 2, given in Chapter 2, that the two parallel vibrations are polarized and nondegenerate while the two perpendicular ones are doubly degenerate and depolarized. If the high and low parallel vibrations are designated by ν_1 and ν_3 , and the high and low perpendicular ones by ν_2 and ν_4 (which will be called system *a*) then in almost all the compounds of the type AB_3 , where B is not a hydrogen atom, the order of magnitude of the Raman shifts from low to high will follow the scheme ν_4 , ν_3 , ν_2 , and ν_1 . If ν_1 and ν_2 are designated as the parallel vibrations (system *b*), the order will be ν_4 , ν_2 , ν_3 and ν_1 . If in AB_3 , B represents a hydrogen atom and the system *a* nomenclature is adopted, then the order may be ν_3 , ν_4 , ν_2 and ν_1 , the lower two frequencies being reversed in a fashion similar to that which has been noted in methane as compared with carbon tetrachloride. If system *b* is used, under the same conditions, the order of course will be ν_2 , ν_4 , ν_3 and ν_1 .

However, the problem of frequency order is not so simple in compounds of the type NH_3 , PH_3 , AsH_3 or in the CH_3 -group. Unfortunately in many of these compounds either the doubly degenerate, perpendicular valence vibration is missing or there is a difference of opinion as to which Raman shift may be ascribed to the ν_2 type of vibration. In ammonia,

FIGURE 19.
Raman Spectra of Some Saturated Aliphatic Hydrocarbons. The height of the lines indicates their relative intensities on a scale of 0 to 10 regardless of the system of designation used by the original authors.



for example, (using system *a*) the ν_2 vibration has been assigned to $\Delta\bar{\nu}$ 3219 and also to $\Delta\bar{\nu}$ 3400. If the last-named assignment is correct then $\nu_2 > \nu_1$ and the relative order of the shifts will be ν_3, ν_4, ν_1 and ν_2 . With system *b*, when $\nu_3 > \nu_1$, the order will be ν_2, ν_4, ν_1 and ν_3 . Howard, Dennison and others consider that for hydrogen derivatives only, either of the last two arrangements indicated above is the correct relative order. This explanation of the usage of specific terms is given some emphasis here because their use in connection with hydrocarbons and their derivatives is a special application. Polarization measurements would probably terminate any doubt as to proper assignment.

According to Dennison's calculations the ν_3, ν_4, ν_1 and ν_2 shifts for the methyl groups are respectively $\Delta\bar{\nu}$ 900, 1400, 2985 and 3120. Only two of these are in fair agreement with the observed values. It may be expected from all these considerations that the ν_1 type of vibration represented by $\Delta\bar{\nu}$ 2985 will be relatively stronger in a centralized molecule such as tetramethylmethane. The spectra of the centralized molecules will be simpler than those of the straight-chain hydrocarbons containing the same number of carbon atoms. It will be seen shortly, however, that $\Delta\bar{\nu}$ 2985 cannot always be assigned to the ν_1 type of vibration. In Figure 19 is shown the comparison spectrum for a large number of aliphatic hydrocarbons wherein the height of the lines represents the approximate relative intensities. The significance of vibrations other than carbon-to-hydrogen will be discussed in succeeding paragraphs.

Glockler and Renfrew⁶¹⁰ attribute the two pairs of lines at $\Delta\bar{\nu}$ 2884, 2941 and 2922, 2963 in liquid ethane to resonance splitting due to the proximity of a first overtone with a fundamental. The first pair originates from the interactions of $2 \times \Delta\bar{\nu}$ 1463 with a hypothetical shift whose mean value is 2913, and the second pair from $2 \times \Delta\bar{\nu}$ 1480 (infrared active only) with the shift whose mean value would be $\Delta\bar{\nu}$ 2943.

The types of vibration in methane and ethane and some of their halogen derivatives have been discussed in some detail in Chapter 5.

The Carbon-to-Carbon Linkage in Ethane and its Homologs

The carbon-to-carbon linkages in these hydrocarbons present a much more complex problem than did the carbon-to-hydrogen linkages. The first carbon-to-carbon linkage is found in ethane, which shows one strong line at $\Delta\bar{\nu}$ 993(5) and a much weaker one at possibly $\Delta\bar{\nu}$ 975(0) which has been attributed to isotopic $C^{12}-C^{13}$ vibrations⁶¹⁰. This vibration refers essentially to the symmetrical oscillation of an individual atom in the direction of a valence bond and is roughly independent of the rest of the molecule except insofar as the strength of this bond may be affected by adjacent groups. This type has been discussed already in considering

the carbon-to-hydrogen vibration. For example, if $\Delta\bar{\nu}$ 993 represents a vibration of the two methyl groups against each other, then this should decrease appreciably if one methyl group is converted to an ethyl group or a still longer radical. This actually occurs in a stepwise fashion up to approximately butane, the values being $\Delta\bar{\nu}$ 867 for propane and 834 for butane. This is an approximate concordance with the increased mass of the components, but the motions giving rise to these frequencies are more complex than a simple vibration of one radical against the other. This progressive decrease, it will be seen later, occurs with the alcohols also.

Karweil and Schäfer consider that ethane has the symmetry D_{3h} and that the frequencies of the fundamentals and their corresponding symmetry classes are: A'_1 , 993, 1344, 2930; A''_1 , 310; A'_2 , 1379, 2955; E' , 827, 1480, 2980; E'' , 1140, 1460 and 2770 cm^{-1} . Crawford, Avery and Linnett record three polarized lines $\Delta\bar{\nu}$ 993, 2900 and 2955 and two faint lines at $\Delta\bar{\nu}$ 620 and 820. Goubeau and Karweil throw in for good measure $\Delta\bar{\nu}$ 786 and 1491 and Glockler and Renfrew believe that the shifts $\Delta\bar{\nu}$ 813 and 1463 observed only in liquid ethane are identical with $\Delta\bar{\nu}$ 827 and 1480 observed in the infrared. This assignment constitutes a violation of selection rules because a molecule with a center of symmetry should have no coincidences with infrared absorption bands. It is suggested that the appearance of these lines originates in an induced asymmetry of the molecule brought about by forces present in the liquid state. Canals and Gastaud state that the C—C lines in all hydrocarbons appearing near $\Delta\bar{\nu}$ 450, 800 or 950 are always polarized.

Whenever a hydrocarbon possesses two or more carbon atoms there are always present what is generally termed transverse vibrations of the C—C linkage which appear below $\Delta\bar{\nu}$ 600 and decrease slightly with each added CH_2 increment. Those lines which lie between $\Delta\bar{\nu}$ 800 and 1100 are usually attributed to the valence vibrations of the C—C linkage, and, as has been mentioned, those in excess of $\Delta\bar{\nu}$ 1100 are first the hydrogen-to-carbon deformation or transverse vibrations, and finally the linear hydrogen-to-carbon oscillations (> 2600).

The C—C shifts for some of the simplest hydrocarbons are given in Table 5 which does not contain all the frequencies reported by different observers.

Simons¹⁴⁴⁷ has calculated the Raman frequencies occurring at less than $\Delta\bar{\nu}$ 1400 from a model having a linear carbon chain configuration. The results are in reasonable agreement with observed values for a long-chain molecule. Each of the calculated frequencies belongs to a definite form of vibration, symmetrical and asymmetrical, of which the symmetrical vibrations are predominant. The total number of Raman lines which appear from any hydrocarbon, it will be remembered, depends on the

Table 5.—The Carbon-to-Carbon Oscillations of Some Simple Hydrocarbons.

Hydrocarbon		Carbon Oscillations in $\Delta\tilde{\nu}$								
Methane										
Ethane					975 (0)	993 (5)				
Propane		377 (2)		867 (10)			1055 (2b)		1155 (2)	
Butane	320 (0)	430 (6)	793 (4)	834 (10)	960 (3)	983 (3)	1060 (6)	1067 (0)	1146 (4)	1303 (3b)
Isobutane	372 (4b)	436 (2b)		796 (10)	967 (5b)				1177 (5b)	1355 (4b)

number of atoms in the molecule, the symmetry of the molecule and the selection rules. The influence of increasing centralization of the molecule on the distribution of the lower carbon-to-carbon shifts is evidenced by the change in the spectra proceeding from normal butane to tetramethylmethane and in the isomeric hexanes as indicated in Figure 19. Kohlrausch⁸²⁷ suggests a constitutional influence in normal butane which can be attributed to a zigzag or a U-shaped chain. Bonino and Manzoni-Ansidei (Raman Jubilee volume) have also investigated the effect of methyl substitution in different positions on chains up to heptane.

For the isomeric paraffins, Kohlrausch and his co-workers believe the chain frequencies to be slightly higher in the branched than in the normal chain compounds. According to Tetetleni the isomeric derivatives are richer in Raman lines and more similar to each other than to the normal compounds.

While the comparison between one compound and a mixture of other members of the same series is fraught with some difficulty, the relation between an individual compound and another compound of the same or different series is in a somewhat different category and may be determined with a reasonable amount of ease.

Free Rotation

This material which has just been presented raises the question of free rotation in compounds of the type of ethane and its 1,2-derivatives. The application of physical and mathematical methods to the problem of free rotation and the existence of *cis* and *trans* isomers originally led to the conclusion that, in the sense postulated by classic organic chemistry, such isomers cannot exist in molecules containing only single bonds. From a theoretical point of view the *trans* configuration has the minimum potential energy. There is, however, some evidence from x-ray diffraction patterns that the *trans* configuration does not exist alone. From the Raman spectra standpoint the *trans* configuration has a center of sym-

metry, and therefore, according to the selection rules, all vibrations which are antisymmetrical to this center of symmetry are forbidden. As the *cis* form possesses no center of symmetry, all the vibrations are allowed in the Raman effect. In consequence of this there should be three polarized Raman lines for the *trans* form and six Raman lines, three of which are polarized, for the *cis*. The total number of frequencies observed for the heavier (carbon) atoms, as well as their polarizations, is intelligible in a general manner if the coexistence of *cis* and *trans* configurations is postulated. Heat capacity data have also thrown some light on this subject, and it has been treated in a general way in Chapter 5.

Cabannes³²⁰ has discussed at some length the question of free rotation around the carbon-to-carbon bond in ethane and its derivatives. Mizushima and his co-workers,^{901, 1118, 1121, 1126, 1137, 1138} and Ananthakrishnan³⁸ have also dealt with this problem recently in considerable detail. Trumpy¹⁵⁹² has concluded that only the *trans* form of 1,2-dichloroethane exists. However, the spectra obtained by him are certainly incomplete. Cheng,³⁶⁶ and Kohlrausch and Ypsilanti,⁸⁸⁸ as well as Mizushima, have concluded that there is a coexistence of two forms of dichloroethane, since more frequencies occur below $\Delta\tilde{\nu}$ 1000 than can be assigned to a single isomer. This is discussed in further detail under the halogen derivatives of the saturated aliphatic hydrocarbons.

Chapter 8

Raman Spectra of Halogen Derivatives of Saturated Aliphatic Hydrocarbons

Halogen Compounds

In a diatomic molecule of the type of hydrogen chloride, bromide or iodide, one would expect a progressive diminution of the Raman shifts with increased mass of the anion. This is realized experimentally, the observed shifts being $\Delta\bar{\nu}$ 2880, 2558 and 2233 respectively. Similarly, in halogen-substituted methanes there is a corresponding progressive decrease in the values for the symmetrical (ν_r) oscillation $X \leftrightarrow CH_3$. For methyl chloride, bromide and iodide the shifts are $\Delta\bar{\nu}$ 710, 600 and 530, and in ethyl chloride, bromide and iodide, they are $\Delta\bar{\nu}$ 654, 566 and 497. The change in masses alone is insufficient to explain this decrease. Harkins and Bowers⁶⁹⁵ calculate what force constants from the simple theory are necessary to balance the equation for the halogen derivatives of methane. These are respectively 3.02, 2.6 and 2.17×10^6 dynes cm^{-1} and hence are much lower than the average value of 5×10^6 dynes cm^{-1} found for the $C \leftrightarrow C$ shift in ethane. Furthermore, the decrease in value from bromine to iodine is only slightly greater than 50 per cent of the decrease between chlorine and bromine. The results are further substantiated by West and Farnsworth,¹⁶⁸⁰ who observe that increasing the length of the chain beyond three carbon atoms causes no further decrease in the longitudinal Raman shift in a homologous series of monohalogen derivatives. This is comparable to the vibrations in the saturated aliphatic hydrocarbons whose equivalent vibrations remain relatively constant in chains exceeding that of butane.

In addition to the wave numbers cited there occurs another series of shifts of lower value, possibly attributable to the transverse (δ_r) motion of the $C-X$ linkage. These are for $R-Cl$ $\Delta\bar{\nu}$ 333, $R-Br$ $\Delta\bar{\nu}$ 280, and $R-I$ $\Delta\bar{\nu}$ 260, although the last item is confined to a few observations.⁴³³ The changes are depicted graphically in Figure 20. The absence of shifts in methyl bromide below $\Delta\bar{\nu}$ 600 is without significance. Practically all those occurring below $\Delta\bar{\nu}$ 800 are attributed to the halogen substitution. By comparing Figures 19 and 20 it will be seen that the presence of a halogen derivative could be detected in a hydrocarbon mixture by means

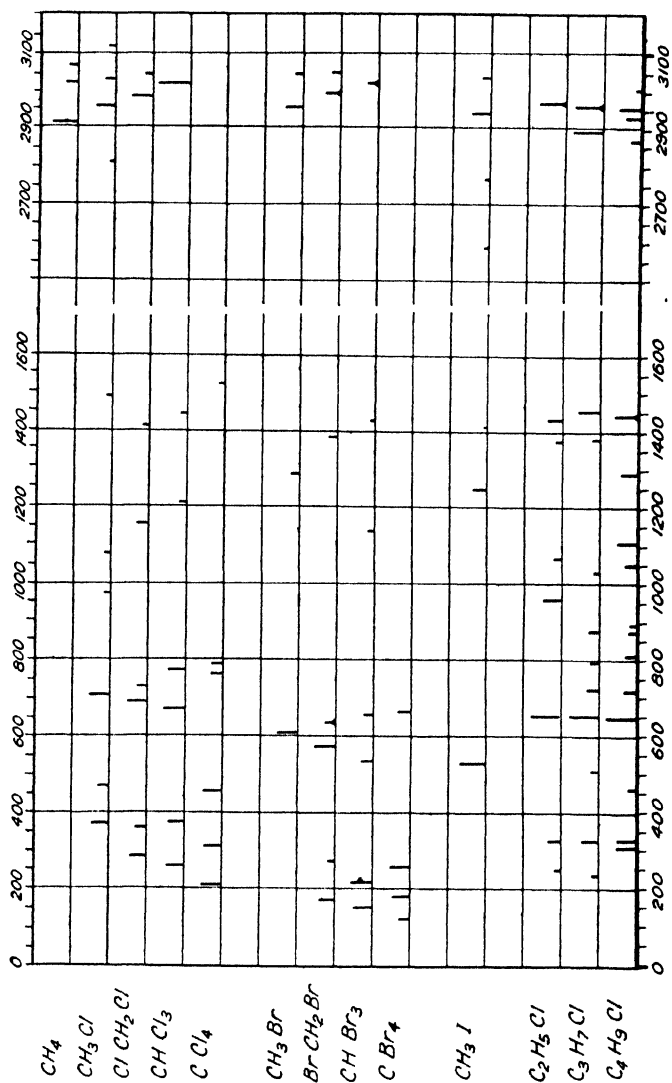


FIGURE 20. Raman Spectra of Some Halogenated Aliphatic Hydrocarbons.

of these characteristic shifts. The effect of increasing halogen substitution on the particular carbon involved in the C—H oscillations is to augment progressively the frequency of oscillation. This is indicative of greater bond strength as the increased mass would diminish rather than enlarge this frequency. On the other hand, when substitution takes place on the α -carbon atom relative to the methyl group, there is little or no effect on the linear hydrogen vibration.

Cleeton and Dufford³⁷⁴ have advanced the hypothesis that the shifts observed are fundamental and combination frequencies. Assuming an unobserved fundamental of $\Delta\bar{\nu}$ 90 as ν_1 , the spectrum of methyl iodide is accounted for as follows:

$\Delta\bar{\nu}$ Observed	$\Delta\bar{\nu}$ Calculated
534	ν_3
2589	$\nu_4 - 4\nu_1$
2771	$\nu_4 - 2\nu_1$
2946	ν_4
3036	$\nu_4 + \nu_2$

where $\nu_1, \nu_2 \dots$ are again somewhat inconsistently but universally used with reference to fundamentals, overtones and combinations. These are numerically equivalent to $\Delta\bar{\nu}$. It is used here in this manner and the results are in fair agreement in this and other cases. As these authors themselves point out, however, calculated results obtained with the *ad hoc* assumption of one or more fundamental frequencies are to be accepted with caution. While there is no doubt that combination frequencies exist in Raman spectra, a quadrupling of a lower frequency is extremely unlikely.

Adel and Barker have reviewed Bennet and Meyers' and Dennison's analyses of the vibrations of the methyl monohalides based on infrared absorption. They apply the wave function

$$\Psi_0 = \Psi'_{(\sigma)} \Psi'^l_{(\rho)} e^{\pm i l \psi}$$

where ν_1, ν_4 and l are the quantum numbers of vibration and $\Psi'_{(\sigma)}$ and $\Psi'^l_{(\rho)}$ are, respectively, the Hermitian orthogonal function with argument σ , and the associated Laguerre orthogonal function with argument ρ^2 , to determine the zeroth order solution of the zeroth order system of vibration. From this they conclude that there is an interaction between vibrational levels at $\Delta\bar{\nu}$ 1460 and $\Delta\bar{\nu}$ 2955, representing the fundamentals ν_4 , and ν_1 , the former combining to $2\nu_4$, which interacts with ν_1 producing a

resonance splitting of energy levels which will account for some of the C—H lines.

The carbon tetrachloride molecule corresponds to a symmetrical tetrahedron (symmetry T_d). The molecule gives rise to five lines at approximately $\Delta\bar{\nu}$ 218, 314, 460, 760 and 780. As is noticeable in Figure 20, at least two shifts apparently correspond to a doublet. This is attributable to the fact that a combination of $\Delta\bar{\nu}$ 459 and 314 yields $\Delta\bar{\nu}$ 773, resulting in a perturbation according to Fermi's hypothesis and consequent splitting of $\Delta\bar{\nu}$ 773 into two lines, $\Delta\bar{\nu}$ 760 and 789. The breadth of these two lines is accounted for by the presence of satellites which owe their origin to transitions from the energy excited states.

Of the nine fundamental vibrations, two are triply degenerate and one doubly degenerate; all of these are depolarized, leaving one symmetrical oscillation which is polarized. The entire relation between symmetry and the number of expected Raman shifts is indicated in the accompanying table where the deformation vibrations are indicated by δ and the valence by ν with various subscripts.

Table 6.—The Effect of Symmetry on the Raman Shifts of Some Halogen Derivatives of Methane.

Compounds	Symmetry	Raman Shifts				
		$\delta_{1,2}$	$\delta_{2,4,5}$	ν_1	$\nu_{2,3,4}$	
CCl_2F_2	C_{2v}	260 ?	320, 433, 450	664	877, 919, 1082?	
CCl_4	T_d	217	313	459	791	
CCl_3Br	C_{3v}	187	243 289	418	710 765	
CCl_2Br_2	C_{2v}	141 164	230 252 318	370	672 720 759	
$CClBr_3$	C_{3v}	239	210 266	326	674 734	
CBr_4	T_d	123 ν_2	183 ν_4	265 ν_1	667 ν_3	

Of course the absence of any line corresponding to a C—H oscillation in carbon tetrachloride is to be expected and the presence of but one line in chloroform at $\Delta\bar{\nu}$ 3016 is obviously due to the C—H vibration, somewhat displaced toward a higher frequency by the influence of the chlorine atoms.

Ananthakrishnan⁴⁰ observes that between 25° and 200° C. the two lines at $\Delta\bar{\nu}$ 760 and 780, forming one of the triply degenerate frequencies, become more diffused with increasing temperature and merge into each other to form a single broad band. The frequency shift at $\Delta\bar{\nu}$ 460, being the symmetrical vibration, is unaffected by temperature. Both the doubly degenerate line at $\Delta\bar{\nu}$ 218 and the triply degenerate one at $\Delta\bar{\nu}$ 314 become broadened with an elevation of temperature.

Landsberg and Malyshev⁹³⁹ have observed combinations of the fundamentals which are explained on the basis of the following scheme:

Carbon Tetrachloride

Fundamentals	Combinations		
A = 217	2A	B + D ₁	D ₁ + D ₂
B = 313	A + B	B + D ₂	2D ₂
C = 458	2B	C + D ₁	C - B
D ₁ = 760	2C	C + D ₂	
D ₂ = 775	A + D ₂	2D ₁	

These second-order rays are about one three-hundredth of the intensity of the first-order rays and are affected markedly by temperature changes.

Wu and Sutherland¹⁷⁴⁰ attribute the diffuse character of some of the Raman bonds in carbon tetrachloride to the effect of chlorine isotopes, and Lord and Blanchard have calculated the entropy of carbon tetrachloride and five isotopic compounds from Raman spectra and electron diffraction data.

Solid carbon tetrachloride according to Sirkar¹⁴⁶⁹ possesses $\Delta\bar{\nu}$ 85 in addition to the usual shifts. The shifts at $\Delta\bar{\nu}$ 760, 780 are much less diffused in the solid.

Crystalline chloroform likewise at low temperature shows some "lattice frequencies," namely $\Delta\bar{\nu}$ 75(1), 94(1), in addition to the splitting of the doubly degenerate frequency at $\Delta\bar{\nu}$ 262 into two components at $\Delta\bar{\nu}$ 263(1), 270(1). The remaining frequencies, $\Delta\bar{\nu}$ 467(2), 666(4), 755(1), 773(1), 1235(0) and 3016(2), approximate the shifts in the liquid, with the possible exception of $\Delta\bar{\nu}$ 467(2), for the solid which appears at $\Delta\bar{\nu}$ 365(5) in the liquid. Some of these changes are attributed to the formation of molecular complexes and to vibrations characteristic of the solid state.

Chloroform-d¹⁷²⁶ possesses $\Delta\bar{\nu}$ 262(3), 366(2), 650(8), 737(2), 908(2), 2256(3). From these data it becomes obvious that $\Delta\bar{\nu}$ 1235 in chloroform is shifted to 908 and that $\Delta\bar{\nu}$ 3019 is shifted to 2256. This last shift is not proportionately reduced according to the square root of the change in mass of D₂ as compared with H₂, as is the case for ν_1 (2914) in methane and ν_1 (2804) in methane-d₄, but is reduced the expected amount if the reduced mass includes the carbon atom in the C—H oscillation. This yields a proportionality factor of 1.36. The diminishing effect of deuterium substitution in the lower observed Raman frequencies is reasonable because the vibrations are concerned primarily with the chlorine and carbon atom movements. The mass effect of deuterium substitution superposed on these oscillations is of small magnitude. This leads to the conclusion that $\Delta\bar{\nu}$ 1235 in chloroform is a shift in which a C—H linkage is directly involved.

Methyl chloride is a symmetrical-top molecule having the symmetry C_{3v}. Of the nine possible fundamental frequencies six come from the

methyl group vibrating with respect to the halogen atom, and these may be treated as a unit; two are doubly degenerate, giving rise to only four observable Raman lines. Of the remaining three, one is doubly degenerate, giving rise to only two Raman lines, or a total of six. Three of the six observable frequencies are parallel vibrations, that is, any change of electric moment associated with such a frequency takes place parallel to the symmetry axis of the molecule. Of the six observable frequencies for methyl chloride, three should be polarized and three depolarized.

From this point of view the types of oscillation represented by ν_3 , ν_6 , ν_2 , ν_5 , ν_1 and ν_4 yield for methyl chloride $\Delta\bar{\nu}$ 712, 1098, 1378, 1450, 2815 and 3024, and for methyl fluoride $\Delta\bar{\nu}$ 1048, 1200, 1460, 1476, 2862 and 2987. The shifts at 2955 for methyl chloride and 2965 for the fluoride represent $2\nu_5$. In this description the three nondegenerate parallel vibrations are represented by ν_3 , ν_2 or ν_1 (in order of magnitude of the Raman shifts) and the three doubly degenerate vibrations by ν_6 , ν_2 and ν_4 respectively. In methyl chloride $\Delta\bar{\nu}$ 712 represents the $\text{CH}_3 \leftrightarrow \text{Cl}$ vibration, $\Delta\bar{\nu}$ 1450 the perpendicular deformation vibration of hydrogen, $\Delta\bar{\nu}$ 1378 the parallel deformation vibration of hydrogen, $\Delta\bar{\nu}$ 1098 the chain deformation vibration (*i. e.*, $\text{A}\uparrow \text{B}\downarrow \text{C}\uparrow$ type, where A represents the chlorine atom, B the carbon atom and C the three hydrogen atoms), $\Delta\bar{\nu}$ 2815 the totally symmetrical valence vibration of the hydrogen atoms along the valence bonds connecting the hydrogen atoms to the carbon atom, and $\Delta\bar{\nu}$ 3024 the asymmetrical or distortional motion of the hydrogen atoms with respect to the carbon atom. The only fly in this ointment is the observation of Cabannes and Rousset ³³⁰ that $\Delta\bar{\nu}$ 2960 has the depolarization factor $\rho \approx 0.05$ corresponding to a parallel vibration, whereas it is represented as $2\nu_5$, where ν_5 is a depolarized perpendicular vibration.

For carbon tetrafluoride ^{174b} three Raman shifts have been observed, namely: $\Delta\bar{\nu}$ 904(10), 437(1), 635(1), corresponding to ν_1 , ν_2 and ν_4 respectively. The shift for ν_3 was estimated to be at $\Delta\bar{\nu}$ 1200. The ν_1 represents the symmetrical oscillation. Glockler and Bachmann report nine fundamentals for dibromofluoromethane.

The only fluorine derivative of ethane thus far investigated is CH_3CF_3 , studied by Hatcher and Yost ⁷⁰¹. The shifts obtained from this compound are: 358(2), 541(2), 603(2), 829(5), 968(3), 1279(1), 1450(4), 2792(2), 2825(1), 2885(1), 2974(5) and 3040(4).

The selection rules, assuming a symmetry C_{3v} , permit for CH_3CF_3 a total of eleven fundamental frequencies of which six would have a value of $\rho \approx 6/7$. It is interesting to note the influence of the C—F group on the C—H frequencies. Particular attention should be called to $\Delta\bar{\nu}$ 3040(4) which represents an unusually high Raman shift for a saturated hydro-

carbon involving the C—H oscillation. As will be discussed later, this is comparable to the C—H frequency in the group =C—H.

It has already been pointed out in an earlier chapter that the restoring forces between atoms in polymatic molecules, along the direction of the valence bonds, cannot be calculated very accurately on the simple harmonic theory. However, Urey and Bradley,¹⁶⁰⁰ by assuming repulsive forces acting between the corner atoms, have arrived at a fairly close agreement between the observed and calculated frequencies in the RX_4 -type of molecule. These forces are assumed to be of the type existing between ions in crystals or inert gas atoms. Terms are introduced into the potential energy proportional to $\frac{1}{r^n}$ where r is the distance between the corner atoms and n may vary from 5 to 9. The final equation contains three constants.

Isomerism and Free Rotation

The lack of free rotation around the C—C bond in ethane derivatives has been mentioned previously. Cabannes³²⁰ has investigated the low-frequency shifts of 1,2-dichloroethane, 1,2-dibromoethane and 1-chloro-2-bromoethane. The results with dichloroethane are given below. The

Table 7.—Isomerism in 1,2-Dichloroethane

ν	$\Delta\bar{\nu}$	i	ρ	Isomer
x^*	124	3	D	
3	264	1	0.52	<i>cis</i>
3	300	6	0.30	<i>trans</i>
2	652	8	0.16	<i>cis</i>
2	752	12	0.41	<i>trans</i>
4	675	2	D	<i>cis</i>
4	(707)	—	—	<i>trans</i>
5	410	2	0.91	<i>cis</i>
x^*	878	1	0.76	
1	941	2	0.14	<i>cis</i> and <i>trans</i>

*Unknown assignment.

frequencies are ascribed to the particular isomers on the basis of polarization measurements and from an analogy with ethylene, since combination spectra appear but rarely.

In this connection it should be mentioned that de Hemptinne (unpublished results) has examined the deuterium derivatives of halogen-substituted ethane. If there were no degeneracy in ethane the total number of fundamental frequencies would be $3n - 6$ or 18. However, because of symmetry considerations in ethane this number of vibrations is reduced considerably. Where symmetry of the molecule is disturbed, as in chloroethane, the number of vibrations is materially increased. In 1-deuterium-

2-halogenethane the theoretical maximum number of vibrations still approaches 18, but the number of shifts observed is in excess of this amount and a large number of lines appear as doublet shifts. This can be accounted for satisfactorily only on the basis of a lack of free rotation and the consequent coexistence of two isomers.

Mizushima and Morino (Raman Jubilee volume) have examined the 1,2-dichloro-, 1,2-dibromo- and 1,2- dibromo- d_2 ethanes in the solid and liquid states. Below the transition points (-65° C for the dichloro-compound and -24° C for the dibromo-compound) there are more Raman lines than above these temperatures. It is shown by means of the isotope effect and by calculation of the normal vibrations that practically all the molecules in these compounds at low temperatures assume the *trans* configuration. It is believed by these authors that if the transitions are caused by the onset of rotation, this rotation must take place about one axis of the zigzag XCCX chain. In compounds of the type $ClCH_2CH_2CH_2X$, where X represents Br, Cl, CN or OH, and in the corresponding bromine compounds, Kohlrausch and Ypsilanti conclude that the halogen frequencies cannot be explained if the molecule exists in only one space form, and that 2,3-dibromobutane appears to exist only in the *trans* form. Trieschmann, on the other hand, from a study of isomers of the latter compound, concludes that the *cis* and *trans* isomers can be distinguished by means of their Raman spectra and other physical properties.

Chapter 9

The Raman Spectra of Aliphatic Alcohols

The application of Raman spectra to the delineation of the structure of the alcohols has not been particularly fruitful. This is primarily because the force constant for C—OH is very much the same as that of C—C, and the relative mass of the hydroxyl group differs from that of a methyl group by only two units. There have been numerous attempts to assign specific Raman frequencies to types of vibrations in the alcohols. In the simpler cases this is undoubtedly a correct procedure. In the more complicated molecules, however, it is exceedingly difficult to distinguish between the vibrations of a hydrocarbon and those of a corresponding alcohol. It is obvious, of course, that the frequency of $\Delta\bar{\nu}$ 1030 which appears in methyl alcohol is analogous to $\Delta\bar{\nu}$ 993 in ethane, and is attributable to the linear oscillation of the hydroxyl group against the methyl group. Furthermore, as with the first members of the hydrocarbon series, there is a decrease in the magnitude of this oscillation with increased chain length. From ethyl to butyl alcohol inclusive, this displacement has the values $\Delta\bar{\nu}$ 885, 856, and 825.

With some alcohols there appears a very broad band, of a width from 80 to 500 wave numbers, which can be resolved into several components; this is undoubtedly caused by the $H \leftrightarrow O$ oscillation. This generally occurs with a maximum near $\Delta\bar{\nu}$ 3400. Unfortunately, however, this can be detected in less than half of the alcohols studied. Landsberg and Ukholin⁹⁴⁵ have followed the augmentation of the $\Delta\bar{\nu}$ 3400 shift with increased temperature and consequently decreased density. Near the critical temperature the principal shift has increased to nearly $\Delta\bar{\nu}$ 3680, or to the shift of an unassociated O—H group. In Figure 21 are given the spectra obtained from a series of aliphatic alcohols, mainly based on the work of Collins,³⁷⁹ Wood and Collins,¹⁷²⁴ Nevgi and Jatkar¹¹⁶⁴ and Kohlrausch.⁸¹⁹ The shifts near $\Delta\bar{\nu}$ 3400 are those observed by Médard.¹⁰⁶⁶

Venkateswaran and Bhagavantam¹⁶⁴⁰ attribute the shifts occurring near $\Delta\bar{\nu}$ 1050, 1240 and 1360 to the C—OH group. The shifts between $\Delta\bar{\nu}$ 1000 and 1250 are so numerous, and so close to those appearing in the normal hydrocarbons, that it is impossible to say with certainty that they owe their origin to the hydroxyl group, although Canals and Gastaud, on the basis of polarization measurements, take the opposite view and assign

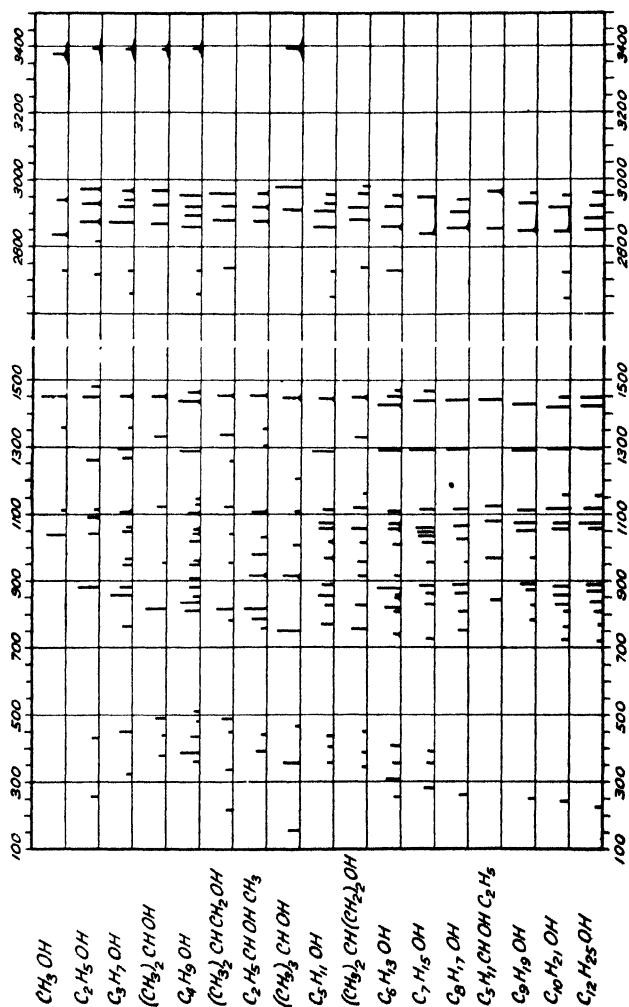


FIGURE 21.

Raman Spectra of Some Aliphatic Alcohols. In some figures a broad and diffuse Raman line is indicated by widening the base of the line in the figure.

the partially polarized line near $\Delta\bar{\nu}$ 1050 to the C—O bond in the alcohols. The shifts near $\Delta\bar{\nu}$ 1450 occur likewise in the hydrocarbons, and are probably due exclusively to the transverse hydrogen vibration. The shifts near $\Delta\bar{\nu}$ 1360 are present in only a few alcohols, and those near $\Delta\bar{\nu}$ 1300 in most hydrocarbons. It is noteworthy, however, that the latter shift undoubtedly is displaced toward a higher frequency in the isomeric alcohols. Furthermore, the spectra from the isomers are apparently more simple than those from the straight-chain compounds. After the molecule reaches a length corresponding to nine carbon atoms there is very little change in the spectra.¹¹⁰

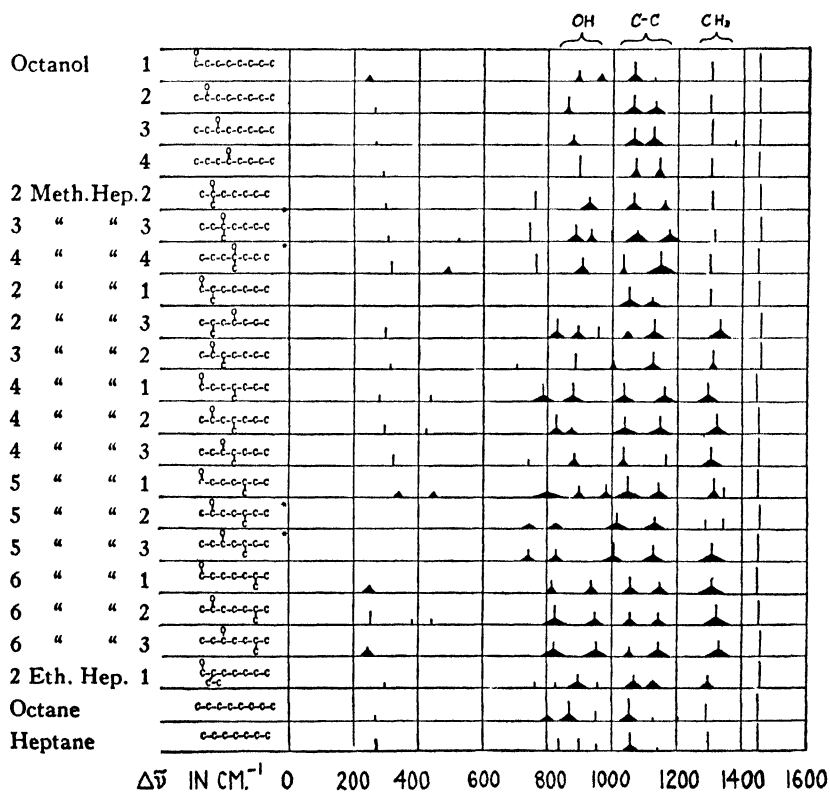


FIGURE 22. Raman Spectra of Some Isomeric Octanols (after Collins).

Nevgi and Jatkar¹¹⁶⁴ assign the frequencies from $\Delta\bar{\nu}$ 2880 to $\Delta\bar{\nu}$ 2960 in the following manner: $\Delta\bar{\nu}$ 2880 is attributed to the longitudinal hydrogen vibration arising from the α -CH, $\Delta\bar{\nu}$ 2930 to the vibration from the β -CH, and $\Delta\bar{\nu}$ 2970 to the end CH-group which is the most free to vibrate. The assignment of $\Delta\bar{\nu}$ 2880 to the α -CH is supported by its absence in tertiary

butyl alcohol, but this conclusion is annulled by the presence of this shift in tertiary amyl alcohol. The $\Delta\bar{\nu}$ 2747 occurring in isobutyl and isoamyl alcohols was attributed by them to the linear oscillations of a hydrogen atom in juxtaposition to two methyl groups. This view seems to be untenable, as this frequency shift occurs in several of the other alcohols which contain no substituted methyl groups.

A large number of octanols whose structures differ only in the relative positions of the methyl and hydroxyl groups have been investigated by Collins.³⁷⁹ The observations were confined to frequencies less than $\Delta\bar{\nu}$ 1500. No two members of this series give an identical spectrum, as is shown in Figure 22. No analysis of these results is entirely consistent. It can be seen that as the hydroxyl group approaches the center of the molecule there is a tendency for the shifts occurring between $\Delta\bar{\nu}$ 200 and 300 to increase progressively. There is also the appearance of a new line at $\Delta\bar{\nu}$ 755 in the branched compounds when the methyl and hydroxyl occur as substituent groups on the same carbon atom. The $\Delta\bar{\nu}$ 1300 may be broad, sharp or a doublet, but this is not consistently related to the structures themselves.

One of the most comprehensive investigations of an individual alcohol was undertaken by Bolla^{192, 193} who observed from ethyl alcohol 56 frequencies, 42 of which are combinations. This leaves 14 fundamental frequencies which are given in Table 8. Titeica¹⁵⁷³ considers that $\Delta\bar{\nu}$ 1273, 2637 and 2876 are combination frequencies.

Table 8.—Fundamental Raman Frequencies from Ethyl Alcohol.

Frequency	$\Delta\bar{\nu}$	Intensities (Basis 100)	Frequency	$\Delta\bar{\nu}$	Intensities (Basis 100)
1	257	2	8	1455	46
2	433	6	9	1618	4
3	814	3	10	2879	59
4	883	60	11	2929	100
5	1051	32	12	2972	61
6	1096	27	13	3240	3
7	1274	17	14	3359	10

By taking all variable factors into consideration it is possible to identify some of the alcohols in mixtures, particularly the isomeric alcohols, when it is not possible to distinguish the alcohols so readily in the presence of some hydrocarbons. Dupont and Dulou⁵⁰⁴ have thus determined the amount of *sec*-butyl alcohol in propyl alcohol obtained by fermentation. Those alcohols which readily yield the $O \leftrightarrow H$ vibrations lend themselves to easy determination. It is possible that shifts near $\Delta\bar{\nu}$ 1050 and 1300 may be connected with a carbon-to-oxygen vibration, but the investigation of characteristic frequency shifts for the alcohols has not led to entirely satisfactory results, owing to the equivalence of the hydroxyl and methyl

groups in the molecule. By ignoring data obtainable from other types of compounds one can justify the specific assignment of certain frequency ranges to the alcohol group, but a precise assignment of frequencies in the $\Delta\bar{\nu}$ 1000–1350 region to alcohols is precarious.

Deuterium Derivatives of Simple Alcohols

The Raman spectra of some of the deuterium-substituted methyl alcohols is given in Table 9 taken from the work of Halford, Anderson and Kissin.⁶⁸³ This demonstrates first, that the symmetrical O—D frequency

Table 9.—The Raman Shifts From Deuterium-Substituted Methyl Alcohol.

CH ₃ OH	CH ₃ OD	CH ₂ DOD
3399		
2987(5)	2987(5)	2979(5)
2942(9)	2946(9)	2948(10)
2914(5)	2917(5)	
2837(10)	2836(10)	2882(9)
		2835(3)
		2686(3)
2588(1)	2591(1)	
	2494	2470
		2237
		2176(7)
1458(4)	1464(5)	1469(4)
1370	1370	
		1343(5)
		1301(6)
	1226(1)	
1171(3)	1179(4)	
1153(1)	1153(1)	
1111(3)		
1056(4)	1071(4)	
1029(6)	1032(6)	1037(7)
	942(2)	894(1)

occurs at approximately $\Delta\bar{\nu}$ 2500, that the C—D frequency appears at $\Delta\bar{\nu}$ 2176(7) and, possibly, that the O—D bending motion is between $\Delta\bar{\nu}$ 900 and 940. Conversely from the presence of specific frequencies in the deuterium compounds, it may be stated that $\Delta\bar{\nu}$ 1464 is, as has been postulated, the bending moment of one of the C—H frequencies. In CH₂DOD the overtone of this shift is displaced, as there is no frequency at $\Delta\bar{\nu}$ 2920 which is present in the alcohol containing a methyl group. In its place are three frequencies, $\Delta\bar{\nu}$ 2948, 2686 and 2835, which may represent overtones of $\Delta\bar{\nu}$ 1469, 1336 and a combination of $\Delta\bar{\nu}$ 1469 and 1336. The shifts $\Delta\bar{\nu}$ 1154(2) and 1056–1071 are absent in the CH₂DOD. On the other hand, $\Delta\bar{\nu}$ 1035 as an average is present in all compounds and may probably be attributed to the C—O linkage.

Doubtless the spectrum of methyl-d alcohol-d is incomplete. If the methyl group is considered as a pyramidal unit there should be four

frequencies present, as noted in the discussion of methyl chloride. Two of these are $\Delta\tilde{\nu}$ 1370(P), 1460(D). The $\Delta\tilde{\nu}$ 2837(D) represents a combination of these shifts and $\Delta\tilde{\nu}$ 2914 an overtone of $\Delta\tilde{\nu}$ 1460. It may be concluded also that $\Delta\tilde{\nu}$ 2940 ($\rho \approx 0.22$), which is unaffected by deuterium substitution, is a fundamental leaving $\Delta\tilde{\nu}$ 2987 ($\rho \approx 0.07$) as the remaining frequency. If this represents the largest perpendicular vibration it should be doubly degenerate and depolarized, which is not the case.

This is supported in part by the fact that methyl fluoride yields $\Delta\tilde{\nu}$ 1048 for the $\text{CH}_3 \leftrightarrow \text{F}$ vibration. If the methyl alcohol molecule closely resembles the symmetrical-top molecule, methyl fluoride, then this vibration should be polarized. Actually, however, since $\rho \approx 0.6$ for this vibration, all these factors lead to the conclusion that the analogy between methyl alcohol and methyl chloride is not as close as might be expected.

After one considers the reduced mass of the carbon, oxygen, hydrogen and deuterium atoms in the simple harmonic equation relating the Raman shifts to the force between the atoms and the reduced mass, then the factor relating the expected frequency from C—D as compared with C—H for example, will not be $\sqrt{2}$ but 1.37. For the O—D and the O—H linkage the factor will be 1.39. This may be more clearly expressed by the following equations:

$$\Delta\tilde{\nu}_{\text{C-D}} \times 1.37 = \Delta\tilde{\nu}_{\text{C-H}}$$

$$\Delta\tilde{\nu}_{\text{O-D}} \times 1.39 = \Delta\tilde{\nu}_{\text{O-H}}$$

Both of these equations express reasonably closely the diminution of the O—D and C—D frequencies as a result of deuterium substitution. This no longer holds for the bending motion of either the C—H and C—D vibrations or for the O—H, O—D bending moment. Assuming that $\Delta\tilde{\nu}$ 942 is the frequency corresponding to the O—D deformation vibration as compared with $\Delta\tilde{\nu}$ 1056 for the O—H one, then, applying the reduction factor calculated from these two quantities (1.12) to the C—D and C—H bending motion, one arrives at the conclusion that the C—D frequency should appear in the neighborhood of $\Delta\tilde{\nu}$ 1305, since $1305 \times 1.12 = 1460$ (C—H). Thus most of the alterations in the spectrum as the result of deuterium substitution are accounted for. These assignments of vibration frequency with modes of oscillations are in general agreement with those of Halford, Anderson and Kissin but differ in some details.

Polybasic Alcohols

The polybasic alcohols have not been investigated in very great detail. The strongest observed shifts with glycol are $\Delta\tilde{\nu}$ 865, 1035, 1465 and 2873. In addition to less intense low frequencies, three other shifts of some

significance appear. These are the doublet frequencies $\Delta\bar{\nu}$ 1070 and 1090 and $\Delta\bar{\nu}$ 3400. These shifts, which occur in most of the alcohols, are probably connected with the R—OH oscillation and the H $\leftrightarrow$ O vibrations respectively. In glycol this last shift, $\Delta\bar{\nu}$ 3400, is much sharper than in water or methyl alcohol, apparently due to the more specific quantization of the vibrational energy.

While the equivalent shift has not been observed in glycerol or propylene glycol, it undoubtedly is present. In Table 10 are given the frequencies

Table 10.—The Raman Shifts Observed from Polybasic Alcohols.

Glycol	341(0)	491(0)	510(0)	660	865(7)	960	1035(5)	1070	—	1090
Propylene Glycol					830(7)	919	1050			
Glycerol		485		690	845(7)	925		1080		
Pentaerythritol		443(2)	510(1)	811(1)	874(5)		1037(3)	1074(6)	1130(2)	
Glycol	1190(1)		1260(3)				1465(5)	2725(1)		
Propylene Glycol										
Glycerol							1455(7)			
Pentaerythritol	1221(0)	1232(5)	1281(2)	1396(2)	1434(3)		1474(4)	2743(3)	2834(2)	
Glycol	2873(6)				2948(6)				3400(2)	
Propylene Glycol			2918							
Glycerol			2910(6)							
Pentaerythritol	2884(0)		2923(9)		2934(4)		2961(10)		3252–3335(2)	

for these compounds from the observations of Whiting and Martin,¹⁶⁸⁴ Howlett,⁷⁶⁷ Morris,¹¹⁴⁰ Hibben,⁷²⁷ Nayar¹¹⁶¹ and Polara.¹²⁵³

The higher members of the series show a tendency toward a marked fluorescence, which decreases rapidly with dilution and increased temperature. The effect is noted by Kutzner⁹³³ in sugar solution and by Hibben^{727, 728} in concentrated phosphoric acid and zinc chloride solutions. This strong, continuous scattering was attributed by Venkateswaran to an effect connected with the viscosity, but Bär⁹³ considered it related to fluorescence. Others believe it arises from impurities. It is certain that fluorescent impurities can be the source of a somewhat continuous spectrum. However, the effect of temperature and dilution in some cases is so marked as to make this less probable as a universal explanation. Hibben has noted that the addition of traces of potassium iodide or nitrobenzene will frequently diminish this effect, which is indicative of deactivation by collisions of the second kind.

Nayar¹¹⁶¹ has compared the spectra of tetramethylmethane, tetramethylsilicon and pentaerythritol. Taking only the carbon atoms into account, a molecule of this type would have tetrahedral symmetry. Rank and Bordner¹²⁸⁸ consider that a strong shift near $\Delta\bar{\nu}$ 730 in the tetramethyl

Table 11. The Raman Shifts Observed from Some Sugars.

Compounds	Raman Shifts									
	416(7)	473(3)	509(2)	537(8)	604(3)					
Xylose										
Glucose		435(3)	519(3)							853(3)
Sorbose	338(1)	388(1)	465(7)	512(8)	607(3)			821(2)		
Arabinose	351(1)	390(3)	435(3)	514(3)	576(2)	695(1)	742(0)	785(1)		872(8)
Galactose	350(3)		433(3)	464(1)	524(2)	615(1)	702(1)			882(2)
Mannose	346(1)		433(3)	464(1)	524(2)	615(1)	702(1)			881(2)
Levulose		404(5)	457(3)	490(2)	523(5)	580(3)	674(1)			
Rhamnose			423(2)	463(3)	520(2)	625(5)	703(3)	780(1)		868(2)
d-Sorbitol	349(1)	398(2)	455(2)	495(2)	529(7)	608(3)	674(3)			884(2)
α-Methyl glucoside	410(1)		450(1)		502(1)					878(8)
α-Methyl mannoside	336(0)	354(0)	420(1)	508(2)	546(3)	666(0)	708(0)	754(2)		846(5)
	312(1)	399(2)	443(1)	466(1)	512(2)	662(1)		820(2)		865(1)
Xylose	900(2)	943(1)	1018(3)							
Glucose	911(2)		1020(2)			1120(8)				1206(0)
Sorbose	902(3)							1145(7)		1200(1)
Arabinose	920(1)	951(1)	1006(8)	1033(1)	1098(7)	1119(7)				
Galactose		950(3)	1018(3)							
Mannose	912(1)	958(3)				1109(5)				1223(1)
Levulose	921(3)					1101(7)				
Rhamnose										
d-Sorbitol						1085(7)				
						1064(5)				
						1075(5)				
						1079(7)				
α-Methyl glucoside	900(5)		1010(5)	1024(5)	1040(5)	1115(5)				1196(0)
α-Methyl mannoside	900(0)	952(5)		1032(4)		1084(5)		1125(5)		1189(1)

compounds represents the "breathing" frequency, or the symmetrical expansion and contraction of the tetrahedron. This frequency has been observed also in camphoric acid¹⁴⁴⁸ which contains a neopentyl group. Some of the other frequencies may be assigned as follows: ν_2 and ν_4 , which correspond to the doubly degenerate and triply degenerate bending types of motion, are represented by $\Delta\bar{\nu}$ 443 and 510. The other triply degenerate oscillation is assigned to $\Delta\bar{\nu}$ 1130, leaving $\Delta\bar{\nu}$ 811 to represent the totally symmetrical vibration. Some of the other frequencies mentioned can undoubtedly be accounted for as harmonics. The O—H band in pentaerythritol is displaced to a lower value than normal, the maximum occurring near $\Delta\bar{\nu}$ 3290. This is considered by some to be evidence of hydrogen bonding.

In view of the intense interest in the constitution of sugars from an organic or biochemical point of view, it is remarkable that they have been so little investigated. Sugars may be considered in part as polybasic alcohols and they exhibit spectra which have some similarity to those of the alcohols.

Wiemann¹⁶⁸⁵ has examined a number of hexitols including *d*-sorbitol. These results and those of other workers are shown in Table 11. All the hexitols examined contain two wide bands near $\Delta\bar{\nu}$ 1080 and 1326. The spectra of xylose, glucose, sorbose, arabinose, galactose, levulose, rhamnose and mannose were also studied. None of these sugars shows any line near $\Delta\bar{\nu}$ 1600–1700, where the carbonyl frequency appears, and consequently any aldehydic or ketonic structure is absent. Shifts occurring near $\Delta\bar{\nu}$ 1050 and 1150 are attributed to the hydroxyl groups, although it should be pointed out that this refers only to the C—O vibration. Furthermore, in any hydrocarbon containing six carbon atoms, lines will also occur between $\Delta\bar{\nu}$ 1000 and 1200. Wiemann attributes the lines near $\Delta\bar{\nu}$ 500 and 800 to the pyran ring.

Hibben⁷⁴² has investigated sucrose, α -methylmannoside and α -methylglucoside. The latter isomers give spectra which are similar in their chain pattern but quite dissimilar in details. This is a case of two very closely related isomers which can be easily distinguished by their spectra, as can be noted in the accompanying microphotometer tracing.

Polara¹²⁵³ has noted a number of C—H shifts between $\Delta\bar{\nu}$ 2016 and 2718 in glucose. Some of these are highly improbable. He also observed a doubtful shift at $\Delta\bar{\nu}$ 1638 which would be assigned to a carbonyl frequency were it actually present.

Prevost has investigated the possible *cis* and *trans* isomerism of some unsaturated glycols.

Chapter 10

The Raman Spectra of Saturated Aliphatic Ethers

There is a fairly strong similarity between the spectra of the alcohols and the corresponding ethers although the lines obtained from the ethers in the region below $\Delta\bar{\nu}$ 1450 are relatively weaker than the equivalent lines in the alcohols. The ethers are alcohols in which the alcoholic hydrogen is replaced by an organic radical, so there is no line corresponding to an O—H frequency. The complexity of the chain vibrations is greater if one compares an alcohol with its methyl ether, for example methyl alcohol with dimethyl ether, since the chain length has been increased by one heavy atom.

As a first approximation, dimethyl ether can be viewed as a nonlinear molecule of the type ABA which would yield three fundamental frequencies, ν_2 , ν_1 and ν_3 , if the four hydrogen frequencies originating in the methyl groups are neglected. Actually there are more shifts observed than can be accounted for on the basis of this simple representation—particularly since none of the observed shifts can be ascribed to harmonic or combination frequencies.

The ethers have been investigated by Lespieau,^{987, 988} Dadiou and Kohlrausch,⁴³¹ Gopala Pai,⁶²⁶ Sirkar,¹⁴⁶⁶ Ganesan and Venkateswaran,⁸⁷⁷ Bär,⁹² Daure,^{455, 456} High⁷⁴³ and others. For the most part attention has been directed primarily to diethyl ether, the observed shifts for which are $\Delta\bar{\nu}$ 375(0), 440(5), 500(0), 840(3), 928(2), 1025(1), 1077(0), 1150(2), 1270(1), 1453(5), 2693(1), 2804(2), 2870(8), 2930(6), 2978(4). For dimethyl ether the values $\Delta\bar{\nu}$ 333(0), 416(0), 930(2), 1102(0), 1160(1), 1455(1), 2814(7), 2869(3), 2920(3), 2955(2), 2990(4) were observed. Dipropyl, diisopropyl, diamyl and diisoamyl ethers have been investigated by High.⁷⁴³ There are no shifts recorded between $\Delta\bar{\nu}$ 1150 and 1450 for diisopropyl and diisoamyl ethers, which makes it easy to distinguish the presence of the iso forms as, with the exception of dimethyl ether, the straight-chain ethers show a notable shift near $\Delta\bar{\nu}$ 1280. In the low-frequency region a fairly strong line occurs at $\Delta\bar{\nu}$ 930 in dimethyl ether, which becomes 840 in diethyl, 790 in isopropyl and 765 in amyl and isoamyl ethers. The principal hydrogen shifts occur at $\Delta\bar{\nu}$ 2865, 2920 and 2960.

Gopala Pai⁶²⁶ has attempted to calculate the valence angle of the oxygen atom in dimethyl ether on the assumption that this ether is a

symmetrical triatomic molecule. If the Raman frequencies $\Delta\bar{\nu}$ 1102, 921 and 416 are considered fundamentals, the calculated valence angle is 102° , as compared with 110° from the electron diffraction pattern. On the other hand, similar calculations for ethylene oxide, assuming $\Delta\bar{\nu}$ 1115, 865 and 810 as fundamentals, yield only a value of 61° for the valence angle. This large decrease is attributed to the valence bond between the two carbons in the epoxy compounds and is supported by the relatively prominent dipole moments of these compounds. Ananthakrishnan³⁸ has determined the relative polarization of the Raman lines in dimethyl ether, while Kohlrausch⁸³⁴ has determined the force constant of the C—O linkage.

Titeica¹⁵⁷³ considers the fundamental frequencies for diethyl ether (corresponding to $\nu_1, \nu_2 \dots$) as $\Delta\bar{\nu}$ 927, 1148, 494, 540, 438, 840, 375 for the C—C and $\Delta\bar{\nu}$ 1455, 2930, 2866, 2978 for the C—H. The combination frequencies are $\Delta\bar{\nu}$ 1038, representing $\nu_3 + \nu_4$, $\Delta\bar{\nu}$ 1077 a higher harmonic of ν_4 and, finally, $\Delta\bar{\nu}$ 1270 a combination of ν_5 and ν_6 .

A series of ethylene oxides has been investigated by Lespieau and Grédy.⁹⁸⁷ The frequencies observed for ethylene oxide are $\Delta\bar{\nu}$ 808(8), 869(8), 1119(5), 1269(7), 2917(7), 2959(7) and 3009(7). The spectrum thus obtained is remarkably different from that of dimethyl ether. This alteration is similar to the alteration in the spectrum of cyclopropane as compared with propane. The hydrogen vibrations occurring at $\Delta\bar{\nu}$ 2917 and 2959 are approximately the same as in dimethyl ether.

In contrast to the absence of any shifts in the 1450 region in ethylene oxide, side-chain substitution in this type of compound produces a plethora of frequencies in this region and, in addition to numerous other frequencies, $\Delta\bar{\nu}$ 3055 for the hydrogen. This value is somewhat lower than the similar frequency in cyclopropane and its derivatives. Apparently for this frequency to appear with considerable strength it is not only necessary to have a triangular ring structure but also to have a side-chain attached to the ring. This is not to be confused with a similar frequency in compounds containing the $=\text{CH}_2$ -group.

For ethylethylene oxide the following shifts are obtained: $\Delta\bar{\nu}$ 405(2), 455(1), 475(1), 732(5), 762(2), 802(2), 835(8), 905(8), 957(1), 1021(1), 1051(1), 1110(2), 1264(9), 1415(2), 1456(6), 1487(2), 2887(2), 2925(10), 2945(10), 2976(5), 3002(5) and 3055(2). The comparison spectra of the ethylene oxides investigated are shown in Figure 24. It can be seen from the numerical values given that the effect of introducing the ethyl group is to produce a number of frequencies in the region between $\Delta\bar{\nu}$ 900 and 1100, $\Delta\bar{\nu}$ 1456 and 1487 as a doublet, and $\Delta\bar{\nu}$ 2887, as well as some additional lower frequencies.

The $\Delta\bar{\nu}$ 2887 is absent in 1,2-dimethylethylene oxide but is present in 1,1-dimethylethylene oxide. The most constant shift in these compounds

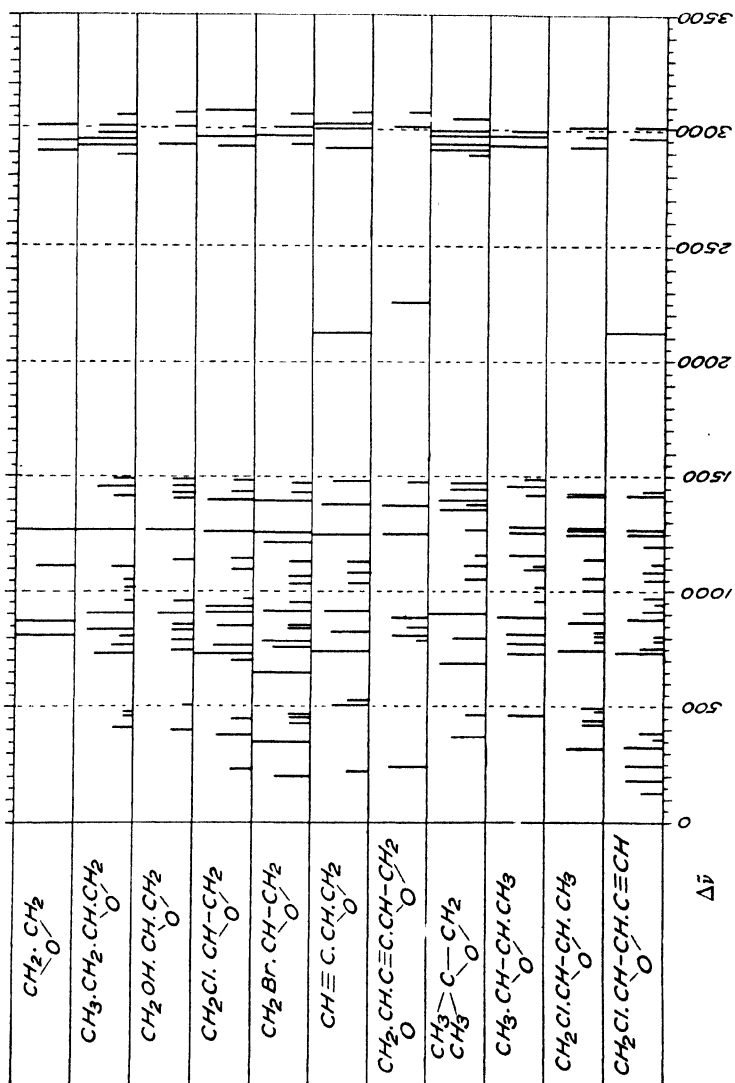


FIGURE 24. Raman Spectra of Some Ethylene Oxides (after Lespiau and Grédy).

is one occurring at $\Delta\tilde{\nu}$ 1265, which is strong and easily identified and remains practically unchanged throughout the series except for a doubling effect. Therefore it must be considered as the most characteristic vibration of this type of ring structure; it corresponds to the shift $\Delta\tilde{\nu}$ 1207 in cyclopropane.

For the disubstituted ethylene oxides, $\Delta\tilde{\nu}$ 1269 becomes a doublet (1256–1277). Lespieau and Grédy attribute this doubling to the presence of two stereoisomers which give a spectrum consisting of two distinct lines. These isomeric forms are:



Kohlrausch and Reitz (Raman Jubilee volume) have compared the spectra of 1,2-dimethylethylene oxide and the unsubstituted ether with the corresponding cyclopropanes and calculated the frequencies for the cyclopropane model with symmetry D_{3h} and ethylene oxide with symmetry I_{2v} . The ν_1 frequency falls near $\Delta\tilde{\nu}$ 1270 for the cyclic ether.

The spectra of the ethers are very close in general to those obtained from the alcohols and hydrocarbons. Nevertheless there are considerable differences in particular lines between the ethers and the other compounds so far described. An interesting example of spectral modification is found in the complex compounds of ethers and alcohols with halides which have been investigated in more detail. Hibben⁷²⁸ noted the interaction of zinc chloride and alcohols. Mixtures of these substances exhibit spectra different from those of the constituents. Wolkenstein and Syркин¹⁶⁹⁶ have studied similarly some oxonium compounds. Dimethyl ether hydrochloride at 280° C., or at lower temperatures, has a spectrum appreciably different from that of dimethyl ether at the same temperatures. The principal change observed is in the frequency which appears at $\Delta\tilde{\nu}$ 921 in ether and at 891 in the hydrochloride. No line was observed which could be attributed uniquely to a $H \leftrightarrow Cl$ vibration. It is believed that none of the ether hydrogen chloride bonds is similar to a hydrogen bond. Briegleb and Lauppe²⁸² observe some difference in the spectra of the oxonium compounds as compared with the parent organic molecules. These are more pronounced in mixtures of alcohols and acids as is shown in Figure 25. Volkenshtein (Wolkenstein)¹⁶⁵¹ observes that sulfur dioxide has a noticeable effect on practically all the shifts observed for dimethyl ether, but mostly on the ν_1 C—O vibration at $\Delta\tilde{\nu}$ 920 and on one of the C—H vibrations at $\Delta\tilde{\nu}$ 2919.

The Raman spectra of alcohols, ethers and hydrocarbons have been shown to vary not only between different homologous series but also

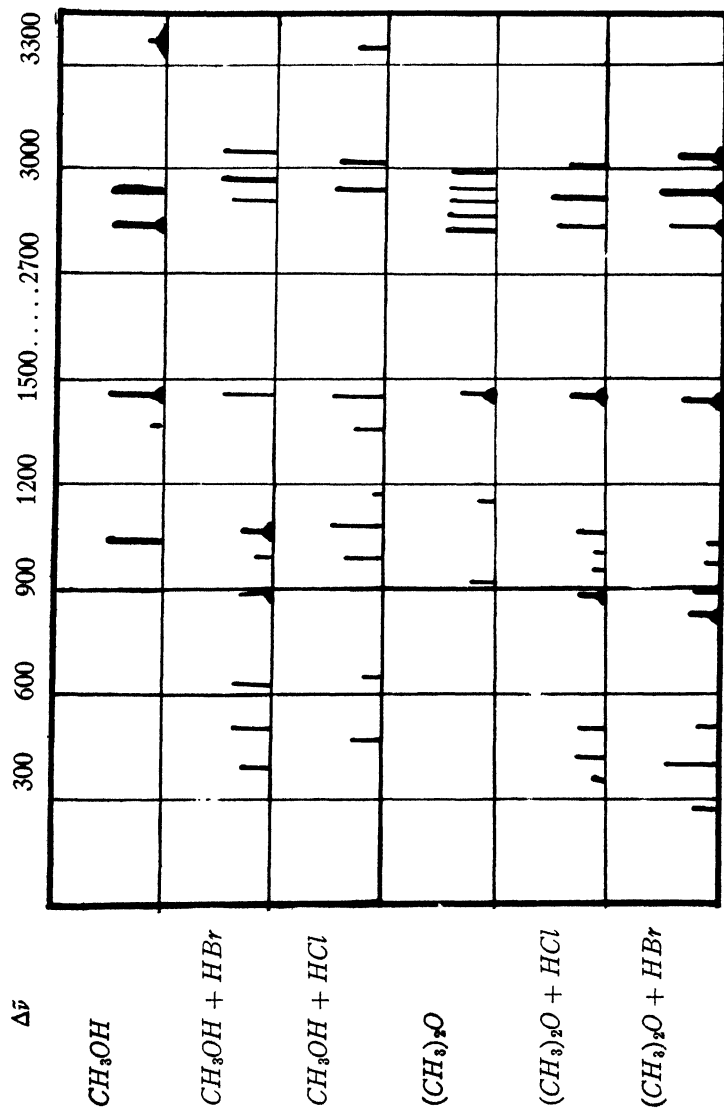


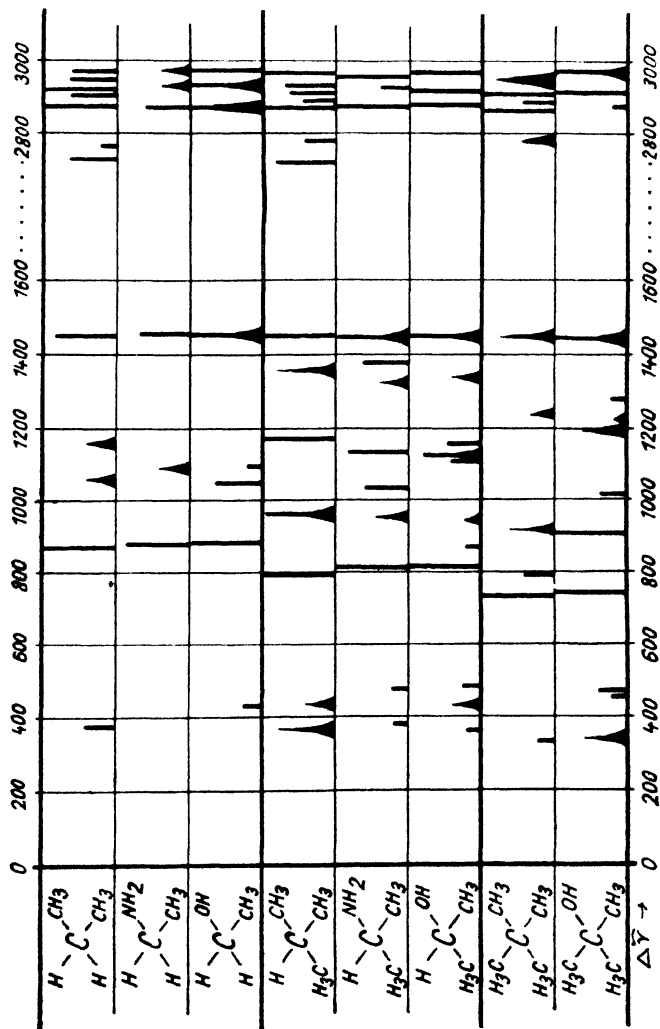
FIGURE 25. Modifications in the Raman Spectra of Some Alcohols and Ethers by Means of Halogen Acids (after Briegleb and Lauppe).

between members of the same homologous series. In the simpler hydrocarbons it is possible to calculate the force exerted between the atomic constituents in the molecules under normal conditions and the relative configurations of the molecules. The effect of substitution on the frequencies is notable and can be calculated if the molecules are not too complex. If the substituent group is markedly different in mass or if the force constant between the carbon atom and the substituent atom or group is markedly different, it has a pronounced effect on the Raman spectrum obtainable from the molecule. This is clear in the case of halogen substitutions. When the mass entering into the force constant remains very much the same it is more difficult, but not impossible, to distinguish the effect of substitution in a not too complicated mixture. Not only does the character of the substituent group affect the general picture but the method of substitution also plays its role, that is, whether substitution increases the length of the chain or increases the centralization. In a few examples this is illustrated in Figure 26, taken from the summary of Kohlrausch, Pongratz and Seka.⁸⁶⁵

As has been pointed out, the replacement of a methyl radical by a hydroxyl group causes little change in the total spectrum because the symmetry is disturbed but little. Other substitutions, such as deuterium in place of hydrogen, give rise to many new lines in addition to those which may be expected as a result of the increased mass. In cases where the Raman frequency is degenerate, that is, where there is a multiple coördinance of frequencies, any replacement in the molecule which will upset the symmetry will result in the appearance of new lines due to the asymmetry thus introduced. Instead of degeneracy, therefore, there may be a splitting of the lines corresponding to the multiple coördinance into two or more components. The equivalence of some of the organic groups is demonstrated on one hand by the absence of such splitting, while on the other hand the lack of equivalence is shown by the appearance of multiple lines. The degree of depolarization may distinguish between the types of vibration which may be the origin of particular frequencies and consequently the origin of changes in degeneracy.

A given hydrocarbon radical in any series will present a more or less constant role irrespective of the variety of groups which may be attached to it. If these groups differ from the hydrocarbon radical in a marked fashion they become the origin of different lines, which may become the basis of compound identification and of great value in interpretation of the structure of these organic compounds. Consequently, in addition to the effects in the types of linkage obtained in the hydrocarbon radicals, there are different effects dependent upon the type of linkage involved in the derivatives of the hydrocarbons. For future considerations the

FIGURE 26.
The Effect of the Central-
ization of Substituent Groups
on the Raman Spectra of
Hydrocarbon Derivatives
(after Kohlrausch, Pongratz
and Seka).



remainder of the treatment of the Raman spectra in hydrocarbons and their derivatives will be based mainly on the effects of these particular types of linkage rather than on the complete spectra. In most cases it is sufficient to illustrate the correlation between Raman spectra and the types of linkage without discussing in complete detail the entire Raman shifts for every compound studied.

Chapter 11

The Raman Spectra of Compounds Containing the Ethylenic Linkage

Ethylenic Compounds

It has been shown that there is a pronounced effect on the types of vibration which may occur in a molecule depending upon the forces between the atoms, the masses of the vibrating constituents and their molecular configurations. In simple cases the methyl group may be considered as a unit and the expected lines calculated from the type of molecular configuration. In other cases it has been shown that other groups may function in a similar manner. This leads to the fundamental expression that, as a first approximation, these groups may be interchangeable as far as some aspects of the Raman spectra are concerned. Nevertheless, there are certain groups which differ widely in mass and possibly in the strength of binding which have a pronounced effect on the single-bond frequency. Urey and Bradley¹⁵⁹⁹ have assumed that not only is there the classic valence attraction between atoms but an exponential repulsion which would account for some of the vibrational frequencies observed in simple molecules.

In the case of the ethylenic linkage, however, irrespective of the types of vibration inherent in the molecule as a whole, there is at least one type of vibration which is characteristic of this type of linkage. This may be modified by substitution; but even when so modified it is still, from an experimental point of view, sufficiently separable from all the other types to be in a category apart. In simple cases this may be considered as the principal oscillation of the ν_2 type. In more complicated cases other factors intervene. Nevertheless, this represents a frequency which is sufficiently characteristic to demonstrate the presence of this type of linkage from a purely empirical point of view.

The Raman spectrum for the ethylenic linkage falls in the region from $\Delta\tilde{\nu}$ 1600 to 1680. The lines are sharp and may be determined with reasonable accuracy. Therefore, the effect of mass and the binding of the atoms in the molecule can be determined with considerable exactness. The reason for this unique displacement is unquestionably connected with the fact that the force constant is very roughly twice that involved in a single

Table 12.—The Raman Shifts from Some Ethylenic Hydrocarbons.

Compound	$\Delta\nu$ 0 to 700	$\Delta\nu$ 700 to 1000	$\Delta\nu$ 1000 to 1500	$\Delta\nu$ 1500 to 1700	$\Delta\nu$ 1700 to 3000	$\Delta\nu$ 3000 to 3200
Ethylene		942	1340(3)	1601 1620(3) 1655	2871	3000(5) 3082(3) 3231 3264
Propylene (incomplete)			1295(8) 1414(6)	1647(8)		3007(7) 3086(7)
Trimethylethylene	253(1) 388(5) 444(5) 528(5)	767(7) 803(2)	1338(7) 1383(7) 1446(7)	1653(1) 1679(8)	2732(1) 2861(8) 2885(2) 2922(10) 2973(8)	3055(2)
1-Pentene	386(5) 427(2) 628(1)	851(5) 881(5) 913(5) 993(1)	1047(2) 1095(2) 1232(2) 1296(8) 1416(8) 1447(7)	1642(8)	2847(3) 2866(3) 2877(8) 2910(8) 2938(8) 2966(5)	3000(8) 3080(8)
2-Pentene	211(3) 412(5) 488(7) 578(3) 698(2)	752(3) 800(5) 860(5) 880(2) 943(3) 966(2)	1027(5) 1066(5) 1248(7) 1268(7) 1290(7) 1310(7) 1379(7) 1450(8)	1658(7) 1674(8)	2857(7) 2887(8) 2920(10) 2941(10) 2966(8)	
1-Hexene	358(2)	818(2) 873(1) 912(2)	1056(2) 1296(7) 1417(8) 1448(7)	1642(8)	2859(5) 2876(8) 2909(8) 2963(5)	3002(8) 3076(5)
2-Hexene (mixture)	389(2)	857(2) 892(2)	1042(2) 1095(5) 1216(1) 1258(5) 1290(5) 1308(7) 1378(5) 1445(7)	1658(5) 1674(7)	2875(8) 2920(8) 2939(7)	
4-Methyl-2-pentene	333(2) 345(2) 484(5)	820(5) 905(2) 956(2)	1043(2) 1103(5) 1256(2) 1300(7) 1380(5) 1456(7)	1659(5) 1673(7)	2870(8)	
3-Methyl-2-pentene (mixture)	320(2) 395(2) 490(5) 551(1)	749(7) 825(1) 125(1)	1071(5) 1117(2) 1255(5) 1317(2) 1350(5) 1383(7) 1451(7)	1673(8)	2852(8) 2879(8) 2920(8) 2966(7)	
2-Methyl-2-pentene	356(5) 473(2) 513(5)	745(5) 816(7) 833(7) 908(7)	1007(5) 1063(7) 1120(2) 1262(5) 1306(7) 1351(5) 1381(7) 1452(7)	1676(8)	2879(8) 2912(8) 2932(8) 2964(7)	

Table 12.—The Raman Shifts from Some Ethylenic Hydrocarbons.—(Continued)

Compound	$\Delta\bar{\nu}$ 0 to 700	$\Delta\bar{\nu}$ 700 to 1000	$\Delta\bar{\nu}$ 1000 to 1500	$\Delta\bar{\nu}$ 1500 to 1700	$\Delta\bar{\nu}$ 1700 to 3000	$\Delta\bar{\nu}$ 3000 to 3200
2,5-Dimethyl-2-hexene (incomplete)		702 769 805 848 949	1107 1264 1328 1376 1445	1669		
3,5-Dimethyl-3-hexene (incomplete)		775 844 956	1032 1120 1282 1327 1380 1450	1667		
3,6-Dimethyl-2-heptene (incomplete)		803 840 953	1025 1108 1330 1381 1449	1668		
4,6-Dimethyl-3-heptene (incomplete)		804 954	1038 1103 1295 1327 1380 1452	1667		
2,3,5-Trimethyl-2-hexene (incomplete)		850 958	1105 1330 1382 1454	1667		
2,4-Dimethyl-2-octene (incomplete)		786 862 955	1103 1163 1295 1328 1377 1450 1465			
2-Methyl-2-octene	187(5) 403(7) 445(3)	761(2) 795(2) 852(3) 893(5) 968(3)	1017(1) 1110(5) 1302(7) 1320(5) 1383(10) 1442(10)	1677(8)	2800(10) 2975(10)	
3-Methyl-2-octene (incomplete)	166(1)		1072(5) 1117(5) 1170(5) 1258(1) 1299(5) 1360(1) 1380(5) 1445(10)	1671(9)	2855(10) 2876(5) 2899(5) 2920(7) 2940(7) 2966(10)	
2,4,6-Trimethyl-3-heptene (incomplete)		702 797 860 956	1102 1165 1300 1329 1377 1449	1665		
2,4,7-Trimethyl-4-octene (incomplete)		952	1098 1283 1329 1375 1448	1663		

bond, and hence carries the emission to a region free from other Raman lines. This opens up an avenue of investigation of constitutional problems where ethylenic linkages are concerned. These may be divided into two classes: those symbolic of the classic ethylenes and their isomers and those occurring in ring structures. The classic shifts, as determined from the ethylenes, may be quite different from those observed in the ring compounds but, nevertheless, they are more similar to the latter than to aliphatic straight-chain hydrocarbons.

Most of this evidence is empirical. This approach is the same procedure, however, by which the "classic" chemist knows that barium sulfate is precipitated on the addition of barium salts to a solution containing soluble sulfates. In whatever category one may wish to classify the method, in either case the net result is one based on experience. The physicist might rest more tranquilly if the cloak of respectability could be placed upon these procedures in the form of potential energy curves or wave mechanical calculations. The probabilities are, nevertheless, that under these circumstances barium sulfate will be precipitated; and likewise the appearance of a Raman shift in the region between $\Delta\bar{\nu}$ 1600 and 1680 is indicative of a double-bond linkage in this type of compound.

In Table 12 are recorded the Raman shifts of several ethylenic hydrocarbons which are incomplete in the sense that some of the relative intensities have not been investigated and that certainly the complete spectra have not been recorded.

On the whole the spectrum obtained from ethylene by different observers is consistent with the C_{2h} symmetry assigned, which should yield six Raman lines. Glockler and Renfrew⁶⁰⁹ have recently observed ten lines in liquid ethylene, most of which were observed previously. A new faint line at $\Delta\bar{\nu}$ 1601 is assigned to the carbon isotope C^{13} . Another new line at $\Delta\bar{\nu}$ 942 was later assigned to a coincidence with $\Delta\bar{\nu}$ 940-950 observed in infrared absorption. The same explanation is given for $\Delta\bar{\nu}$ 3075 while $\Delta\bar{\nu}$ 2997 is considered a modification of $\Delta\bar{\nu}$ 3008 because of the presence of the carbon isotope C^{13} . The modes of vibration are discussed in Chapter 5 and the effect of deuterium substitution is dealt with under the subheading of *cis-trans* isomerism. It has been observed that substitutions may affect the ethylenic linkage in compounds of the type $CH_2=CHR$. This is illustrated in Tables 13 and 14. Here it is shown that hydrocarbon substitution in ethylene causes a profound modification in the $C=C$ frequency occurring at $\Delta\bar{\nu}$ 1620 so as to elevate it to approximately $\Delta\bar{\nu}$ 1642, and that further hydrocarbon substitution produces only a negligible effect. There is a notable diminution in some of the constant frequencies when the substituent group is a halogen or an aldehyde group. This decrease in magnitude pertains chiefly to the ethylenic frequency.

Table 13.—The Raman Shifts Characteristic of the Ethylenic Linkage and other Shifts Common to Olefins

Substance	$\Delta\bar{\nu}$				
$\text{CH}_2=\text{CH}\cdot\text{H}$		1340		1620	3000
$\text{CH}_2=\text{CH}\cdot\text{CH}_3$	1295		1414	1647	3007
$\text{CH}_2=\text{CH}\cdot\text{C}_2\text{H}_5$	1294		1416	1642	3003
$\text{CH}_2=\text{CH}\cdot\text{C}_3\text{H}_7$	1296		1416	1642	3001
$\text{CH}_2=\text{CH}\cdot\text{C}_4\text{H}_9$	1295		1416	1642	3002
$\text{CH}_2=\text{CH}\cdot\text{C}_5\text{H}_{11}$	1299		1416	1642	3000
$\text{CH}_2=\text{CH}\cdot\text{C}_6\text{H}_{13}$	1296		1416	1642	3001
$\text{CH}_2=\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$	1296		1413	1642	3006
$\text{CH}_2=\text{CH}\cdot\text{C}_7\text{H}_{15}$	1300		1416	1642	3003
$\text{CH}_2=\text{CH}\cdot\text{CH}_2\cdot\text{C}\equiv\text{C}\cdot\text{C}_6\text{H}_5$			1416	1642	
$\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{OH}$	1290		1416	1646	3014
$\text{CH}_2=\text{CH}\cdot\text{CHOH}\cdot\text{CH}_3$	1287		1416	1646	3013
$\text{CH}_2=\text{CH}\cdot\text{CHO}$	1277		1363	1618	
$\text{CH}_2=\text{CH}\cdot\text{COOH}$	1288		1397	1638	3111
$\text{CH}_2=\text{CH}\cdot\text{Cl}$	1271		1355	1608	3036
$\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{Cl}$	1291		1411	1640	3022
$\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{Br}$	1295		1409	1635	3016
$\text{H}_2\text{C}=\text{CH}\cdot\text{CH}=\text{CH}_2$	1277		1436	1634	3000
$\text{H}_3\text{C}\cdot\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}_2$	1288		1443	1646	2998
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\cdot\text{CH}=\text{CH}_2$	1291		1420	1640	3012
$\text{H}_2\text{C}=\text{CHCH}_2\text{CH}=\text{CH}_2$	1295		1413	1644	3010
$\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	1298		1416	1641	3004

Table 14.—The Effect of Disubstitution on $\text{C}=\text{C}$ Shifts.

Radical R	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-$			Radical R	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-$		
	$\text{CH}-\text{R}$	cis	trans		$\text{CH}-\text{R}$	cis	trans
CH_3	1647			$\text{CH}_2\text{C}\equiv\text{CC}_6\text{H}_5$	1642		
$\text{CH}_3\text{O}(\text{COCH}_3)$	1649	1665	1679	CHClCH_3	1640		
CH_2OH	1646	1658	1677	$\text{CH}_2\text{C}_6\text{H}_5$	1640		
CHOHCH_3	1646			CH_2Cl	1640		1671
$\text{CHOHC}\equiv\text{CH}$	1646		1676	CHCl_2			1666
$\text{CHOHCH}=\text{CH}_2$	1646		1674	CHBrCH_3	1635	1651	1666
C_2H_5	1642	1658	1674	COOH	1638	1645	1652
C_3H_7	1642	1658	1674	COOR		1644	1655
C_4H_9	1642	1658	1674	C_6H_5	1631	1642	1665
C_5H_{11}	1642	1658	1674	H	1620		1647
C_6H_{13}	1642	1658	1674	CN		1628	1645
C_7H_{15}	1642			CHO	1618	1625	1642
$\text{CH}\begin{cases} \text{CH}_3 \\ \text{CH}_3 \end{cases}$		1659	1673	Cl	1608		
$\text{CH}_2\text{C}_6\text{H}_9$	1642	1658	1674	Br	1598		
$(\text{CH}_2)_3\text{C}_6\text{H}_{11}$		1657					

Bourguel^{262, 264} and Bourguel and Piaux²⁷² have made systematic studies of the ethylenic compounds and have concluded that the hydrocarbon radicals react on the $\text{C}=\text{C}$ linkage in the opposite sense, that is, tend to increase the ethylenic shift. Bourguel²⁶² notes that the effect of disubstitution also increases it, but this augmentation is less if the two groups are on the same rather than different carbon atoms. For example, in 2-pentene and 2-methyl-1-butene $\Delta\bar{\nu}$ 1657 and 1652 are observed. It is notable that the halogen, aldehyde, acid and ester radicals decrease the

normal frequencies of isomers. Kirrmann (Raman Jubilee volume) has added to the knowledge of substituted unsaturated esters.

In the trisubstituted ethylenes such as trimethylethylene, the $C=C$ frequency occurs near 1675, which is similar to the value observed for the *trans* isomer in the disubstituted derivatives. There is here also a diminution caused by the addition of the negative radicals such as halogens and those others previously named. Grédy^{651, 657} has summarized these conclusions in regard to disubstitution and Risseghem, Grédy and Piaux¹³⁸¹ and Grédy⁶⁵² have obtained results with trisubstituted ethylenes which are summarized in Table 15.

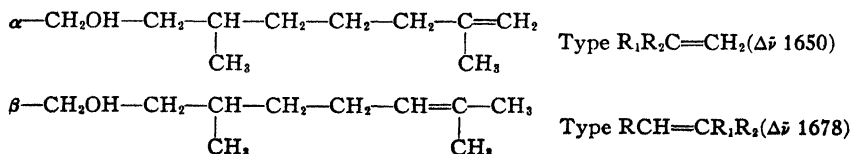
Table 15.—The Effect of Trisubstitution on $C=C$ Shifts.

Compound	$\Delta\bar{\nu}$	Compound	$\Delta\bar{\nu}$
$(CH_3)_2C=CHCH_3$	1679	$CH_2Br \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHCH_3$	1648
$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHCH_3$	1673	$Br \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHCH_3$	1648
$C_2H_5 \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHCH_3$	1671	$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHCH_3$	1647
$C_6H_{13} \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHCH_3$	1676	$CHO \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHCH_3$	1645
$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHC_2H_5$	1677	$C_2H_5 \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHCH_3$	
$(CH_3)_2C=CHC_6H_{11}$	1676	$CHO \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHCH_3$	
$(CH_3)_2C=C(CH_3)_2$	1658	$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHC_2H_5$	
$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHCH_3$		$CHO \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHC_2H_5$	
$Br \begin{array}{l} \diagup \\ \diagdown \end{array} C=CHCH_3$			

The general postulate that halogen substitution causes a diminution of the ethylenic frequency is somewhat vitiated by the fluorine-substituted unsaturated compounds. These are apparently in a separate category like most fluorine compounds. In $CF_2=CCl_2$ the ethylenic shift is $\Delta\bar{\nu}$ 1735(6), according to Hatcher and Yost.⁷⁰¹

Some examples may be given as to the practical use of these data as far as the determination of some types of molecular structure is concerned, even though it will be seen later that these applications have a much wider utility than is indicated in these illustrations.

It has been found that compounds of the type 2-methyl-1-octene yield $\Delta\bar{\nu}$ 1647 and those of the type 3-methyl-2-nonene yield $\Delta\bar{\nu}$ 1672. These are analogous to the α and β forms of the compounds generally known as rhodinol and citronellol, the formulas of which are given below:



From this it is concluded that the β form ordinarily predominates in citronellol. Desreux and Dulou state that citrol ordinarily contains no α form, while citronellol is a mixture of the β and the α forms.

A typical example of the demonstration of polymerization is obtainable from the studies of Signer and Weiler,¹⁴²⁹ Hibben,⁷³⁵ Mizushima, Morino and Inoue¹¹³⁵ and Monnier, Susz and Briner. In the first case all of the Raman shifts of styrene, polystyrene, and ethyl benzene were contrasted, and in the second methyl methacrylate and its polymers were compared. It can be readily seen that the aliphatic C=C present in styrene is absent in ethyl benzene and polystyrene. The entire analysis is consistent with the view that the styrene molecules are coupled through a breakdown of the double bond in the side-chain to form long chains of polymerized molecules.

The mechanism of polymerization of an ethylenic compound has been studied by Hibben⁷³⁵ in the case of methyl methacrylate. The spectrum of the polymerized compound is radically different from that of the monomer. Chief among these differences is the disappearance of the ethylenic shift, indicating that the polymerization is brought about *via* this group. There are, however, other differences which are notable. These are the appearance of a low frequency shift at $\Delta\tilde{\nu}$ 300; a decrease in the relatively strong frequency occurring in the liquid at $\Delta\tilde{\nu}$ 835 to 806, and a modifica-

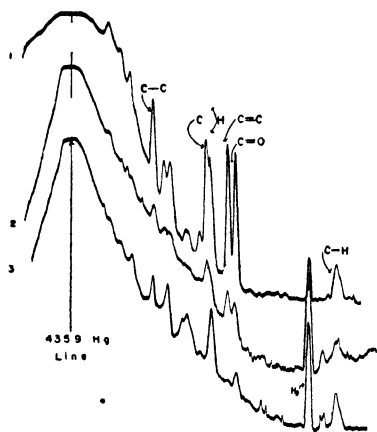


FIGURE 27. Raman Spectra of Methyl Methacrylate in Different States of Polymerization. Line 1 represents the monomer, Line 2 the partially polymerized monomer and Line 3 the solid polymer.

tion of the doublet frequencies occurring in the liquid at $\Delta\tilde{\nu}$ 940, 1008, 1404, 1451, to a singlet shift at 974 and 1448. These results are shown in Figure 27. Both the ethylenic and carbonyl frequencies occur at much the same positions as those observed with maleic and fumaric esters. The intensity relations, however, between these two shifts are closer to the

fumaric derivative than to the maleic. It is to be pointed out from the results observed by Hibben⁷³⁵ that a small amount of polymerization does not modify appreciably the total spectrum, while at the same time the viscosity increases enormously. In other words a small amount of polymerization may alter the physical characteristics of the liquid to a great extent without altering more than a small fraction of the molecular constituents.

Raman effect determinations are capable of an accuracy of a fraction of a wave number. In general, this is not always necessary because the aggregate effect is obvious. Under more accurate conditions and measurement the possibilities of alteration in the ethylenic frequency as a function of substitution are virtually unlimited. Under ordinary conditions this much at least is true: that there is a change on substitution, and the magnitude of this change is dependent on whether the substitution is on the carbon atom directly connected to the ethylenic linkage or is in the α -position to that carbon atom. The modification resulting from the α -substitution is much less than the direct substitution, which is in agreement with the classic view of organic chemistry.

Other frequencies, characteristic of the binding between other atoms, likewise may be altered. In general, the hydrogen frequencies appearing near $\Delta\bar{\nu}$ 3003 and 3080 are modified. In fact, these particular C—H frequencies occur principally in compounds possessing hydrogen atoms attached to a double-bonded carbon atom.

Other unsaturated compounds, such as cycloölefines and aromatic compounds, possess somewhat different $=\text{C—H}$ or $=\text{CH}_2$ shifts between $\Delta\bar{\nu}$ 3000–38. The epoxy ethers, derivatives of cyclopropane and substituted amines also yield C—H shifts greater than 3000. The intensity relations make it very easy to distinguish between hydrogen atoms attached to a double bond and hydrogen atoms in a triangular ring structure without a double bond.

Cis-Trans Isomerism

The compounds given in Table 13 are essentially those of the type R—CH=CH_2 . The question now is, What effect do substitutions of the type R—CH=CH—R have on the C=C shift? This brings immediately to the fore the problem of *cis-trans* isomerism. The isomers of this type examined earliest were the 1,2-dichloroethylenes studied by Bonino and Brüll,²¹⁷ and the geometrical isomers, ethyl fumarate and ethyl maleate, which were investigated by Ffolliott,⁵⁵⁰ and more recently by Hibben.⁷³⁵ Pestemer,¹²¹⁹ and Dadieu, Pongratz and Kohlrausch^{438, 440, 441, 442} have also considered the *cis-trans* isomerism in halogen and oxygen derivatives of ethylene. In Table 16 are given the results compiled by Cabannes⁸²⁰

for 1,2-dichloroethylene. It is to be observed that there is considerable difference between the spectra of these two compounds.

The frequencies and types of vibration shown schematically (primes indicate hydrogen oscillations) do not correspond to all the observed frequencies, but only to the fundamental ones. Those shown in horizontal column one are the polarized or partially polarized vibrations. The first

Table 16.—The Raman Shifts from *Cis* and *Trans* 1,2-Dichloroethylene.

<i>Cis</i>					
1.	$\Delta\bar{\nu}$ 3077 ρ 0.27 i 10	711 0.06 10	1586 0.19 8	174 0.52 8	1179 0.69 6
2.	$\Delta\bar{\nu}$ 406 ρ 0.85 i 5	561 0.89 3	875 D 1	?	?
<i>Trans</i>					
3.	$\Delta\bar{\nu}$ 351 ρ 0.29 i 10	1271 0.21 7	3070 0.20 6	1576 0.10 5	848 0.09 3

three of these are strongly polarized, are the most intense, and represent respectively the $C \leftrightarrow H$, $C \leftrightarrow Cl$ and $C=C$ valence vibrations. In column two are shown three observed antisymmetrical vibrations, all of which are depolarized, thus establishing the symmetry C_{2v} , and eliminating any possibility of the symmetry C_{2h} for the molecule, which would yield six polarized Raman lines. The ν_6 vibration should appear near $\Delta\bar{\nu}$ 1300 and ν_4' near $\Delta\bar{\nu}$ 3100, but neither is observed. The weak band found at 3158 in the *cis* isomer is considered as a harmonic of $2\nu_1$. Likewise $\Delta\bar{\nu}$ 809 and

1688, not included in the table, are assigned respectively to $2\nu_6$ and $2\nu_4$. In the table the shifts are arranged in the order of decreasing intensity.

In horizontal column 3 are the observed fundamental shifts for *trans* dichloroethylene. It is notable, first, that all these are polarized because of the greater symmetry of the *trans* configuration and, secondly, that the intensities follow a different order. In the *cis* compound $\nu'_2, \nu_2 > \nu_3, \nu'_3$ while in the *trans* compound $\nu_3, \nu'_3 > \nu'_2$ and ν_2 . The only depolarized lines in the *trans* modification are $\Delta\bar{\nu}$ 3142 which is a harmonic ($2\nu_1$) and 766 ($2\nu_6$). The lines $\Delta\bar{\nu}$ 1693 and 1630, which are very weak and polarized, may be the result of $2\nu_4$. In the *trans* compound, unlike the *cis*, the fundamentals ν_4 and ν_5 are inactive. This appearance of harmonics when the fundamental is forbidden is not unusual. These assignments are disputed. Calculations of the expected frequencies, while interesting, do not agree any too reasonably with the observed ones.

In 1,1-dichloroethylene it is notable that the valence $C \leftrightarrow Cl$ vibration is $\Delta\bar{\nu}$ 600(10)(P) as compared with $\Delta\bar{\nu}$ 711 for the *cis* and 848 for the *trans* compounds. This line would seem to be a good means of distinguishing between these isomers. On the other hand ν'_3 and ν_1 are shifted to a higher value, $\Delta\bar{\nu}$ 1393 and 1611. Parenthetically it may be said that the spectrum of 1,1-dichloroethane bears a closer resemblance to dichloromethane than to dichloroethylene. It will be seen shortly that in most *trans* derivatives the $C=C$ or ν_1 type of vibration occurs at a higher frequency than in the *cis* compound. In the hydrocarbons, however, on account of the multiplicity of lines in the lower frequency regions, it is much more important to ascertain if there is an effect on the ethylenic linkage which can be clearly observed. Bourguel, Grédy and Piaux²⁶⁹ have examined a number of *cis* and *trans* isomers. The results are indicated in Table 17. The ethylenic

Table 17.—The Raman Shifts from *Cis* and *Trans* Isomers of Unsaturated Hydrocarbons.

Compound	$\Delta\bar{\nu}$		
<i>cis</i> -2-Pentene	1248-1266(7)	1375(2)	1658(10)
<i>trans</i> -2-Pentene	1298-1313(7)	1378(7)	1674(10)
<i>cis</i> -2-Octene	1256(7)	1376(2)	1658(10)
<i>trans</i> -2-Octene	1305(7)	1379(7)	1673(10)
<i>cis</i> -2-Nonene			1658(10)
<i>cis</i> -2-Cyclohexyl-6-hexene	1260(7)		1657(10)
<i>cis</i> -1-Phenyl-1-propene	1192(7)	1373(2)	1642(10)
<i>trans</i> -1-Phenyl-1-propene	1210(7)	1378(7)	1664(10)

compounds of the type $R-CH=CH-R'$ yield $\Delta\bar{\nu}$ 1658 for the *cis* compound and 1674 for the *trans*, when R and R' are alkyl radicals. If R' is a phenyl group in lieu of an aliphatic radical, the $C=C$ shift is decreased and becomes $\Delta\bar{\nu}$ 1642 for the *cis* forms and 1664 for the *trans*. The band near $\Delta\bar{\nu}$ 1256 in the *cis* compounds is increased also in the *trans* to $\Delta\bar{\nu}$ 1300.

This work has been extended by Grédy,^{651, 654, 655, 656, 657} Grédy and Piaux⁶⁵⁸ and Grédy and Risseghem⁶⁶⁰ who have studied a number of *cis* and *trans* isomers. These include crotonyl acetate, methylvinylcarbinol acetate, crotonyl alcohol, methylvinylcarbinol, amylvinylcarbinol, crotonaldehyde, 1-methylallyl bromide, 2-butenyl bromide and other compounds. Some of these compounds were mixtures of isomers and show both *cis* and *trans* spectra. Crotonaldehyde and crotonyl alcohol yield respectively $\Delta\bar{\nu}$ 1647 and 1677 for *trans*, with 1625 and 1657 for *cis*. Crotonyl acetate and 2-butenyl bromide show $\Delta\bar{\nu}$ 1679 and 1665 *trans* with 1664 and 1661 *cis*. Methylvinylcarbinol, methylvinylcarbinol acetate and 1-methylallyl bromide yield respectively $\Delta\bar{\nu}$ 1647, 1648 and 1638.

Recently Gershinowitz and Wilson⁵⁹⁷ have determined both the infrared and Raman spectra of *cis* and *trans* 2-butene. If the methyl groups are considered as units, the *trans* compound has a center of symmetry and there should be no coincidences between the Raman and infrared spectra except by accident, while in the *cis* compound some frequencies should be active in both the Raman effect and infrared. This is realized experimentally. From *cis* 2-butene some twenty lines are found and from the *trans* isomer fourteen, of which about half are polarized. The most intense C—H shift in the *trans* compound is at $\Delta\bar{\nu}$ 2926(10)(D), while 2867(5) is polarized. Other hydrogen shifts of uncertain polarization are 2739(2), 2965(4) and 3011(2). In the *cis* compound these shifts occur fairly near these values, but with greater intensity. This isomer also possesses a number of other weak hydrogen lines. It differs from the *trans* modifications chiefly in the shifts less than $\Delta\bar{\nu}$ 900, and in view of the fact that the C=C shift for *cis* 2-butene is $\Delta\bar{\nu}$ 1669 and for *trans* $\Delta\bar{\nu}$ 1681.

Trumphy¹⁵⁸⁵ has examined the deuteriumdichloroethylenes, finding little difference in the ethylenic frequencies, but a considerable difference in those frequencies which may be ascribed to C—H, corresponding to either symmetrical or asymmetrical vibrations.

According to Trumphy¹⁵⁹¹ the strength of the C—D binding in the *cis* and *trans* dichloroethylene-d₂ and in tetrachloroethane-d₂ is slightly greater than in the corresponding hydrogen compounds. This is to be compared with the C—H frequency ($\Delta\bar{\nu}$ 2984) in tetrachloroethane, which becomes $\Delta\bar{\nu}$ 2240 for C—D in tetrachloroethane-d₂. Similarly in dichloroethylene and in dichloroethylene-d₂ the C—H and C—D shifts are $\Delta\bar{\nu}$ 3080 and 2325 respectively.

The deuterium derivatives of ethylene have been investigated carefully by Delfosse, Jungers, Lemaitre, Tchang and Manneback,⁴⁷¹ de Hemp-tinne, Jungers and Delfosse,^{715, 716} Lemaitre, Manneback and Tchang,⁹⁷⁹ Manneback,¹⁰¹⁶ and Manneback and Verleysen.^{1017, 1018} These authors have attempted to develop a theory of the vibration spectrum of ethylene

and have deduced from the experimental data values for some of the force constants occurring in the potential energy function of the molecules. Bonner²⁵⁷ also has added recently to the knowledge of the vibrational spectrum of ethylene. The use of deuterium substitution provides a larger number of Raman shifts by means of which the theoretical deductions may be checked.

Reference already has been made to the fact that the types of vibration found in ethylene are given in Figure 16 in Chapter 5. In ethylene-d₄ these modes of course are unaltered. The total number of possible vibrations for these compounds is twelve, of which six occur as fundamental frequencies in the Raman effect. In ethylene the three parallel vibrations are $\Delta\bar{\nu}$ 1342, 1623 and 3019 which are illustrated in Figures 16*b*, 16*c*, and 16*a* respectively. The first of these represents the totally symmetrical deformation vibration of the hydrogen atoms and the latter two the totally symmetrical valence vibration of the C=C and C—H groups respectively. The perpendicular vibration of the hydrogen atoms in the CH₂-group, illustrated by Figure 16*j*, occurs weakly near $\Delta\bar{\nu}$ 3200. The other two Raman lines which may occur are the deformation vibrations shown in 16*k* and 16*l* corresponding to $\Delta\bar{\nu}$ 950 and 1200. The entire six frequencies have not been observed by all workers; particularly is this true of $\Delta\bar{\nu}$ 1200. Only recently the shift near $\Delta\bar{\nu}$ 3200 has been found. This lies so close to the harmonic of the C=C oscillation that its existence is open to some question. Some authors have assigned a frequency which may occur near $\Delta\bar{\nu}$ 3070 rather than $\Delta\bar{\nu}$ 3200 to the asymmetric hydrogen oscillation.

In ethylene-d₂ there are three possibilities of compound formation. These are *cis*-, *trans*-, and *asym*-ethylene-d₂. The number of coincidences of the Raman spectra frequencies with those active in infrared absorption for these compounds depends on the symmetry. In ethylene-d all the vibrations should be active in both Raman spectra and infrared absorption. In the case of *trans*-ethylene-d₂ a center of symmetry permits the separation of the frequencies into two groups, one symmetrical and the other antisymmetrical with respect to the center, the symmetrical vibration alone being Raman active. For the *cis*- and *asym*- isomers the vibrations from ethylene-d₂ can be divided also into two groups, symmetrical and antisymmetrical, with respect to their planes of symmetry, all the frequencies being both Raman and infrared active. The observations and theoretical calculations of the authors named in the beginning of this discussion are both supplementary and partially independent. There is reasonably good agreement among all of them and for this reason only one of the most recent publications⁷¹⁶ will be used to provide slightly more detailed results. In the accompanying table are shown some of the results obtained by de Hemptinne and his co-workers together with the values as calculated by

Table 18.—Some of the Calculated and Observed Raman Shifts in Various Deutero-ethylenes.

		C_2H_4		C_2D_4		$\text{C}_2\text{H}_2\text{D}_2(cis)$		$\text{C}_2\text{H}_2\text{D}_2(trans)$		$\text{C}_2\text{H}_2\text{D}_2(asym.)$					
		Calc.	Obs.	Calc.	Obs.			Calc.	Obs.	Calc.	Obs.				
S_1	ν_1	1621	1620	1428	1514	π_ν	1516	1567	S	1515	1567	π_x	1555	1581	ν_1
	ν_2	3019	3007	2283	2251		3065	3046		3049	3033		3004	ν_2	
	ν_3	1344	1341	1009	981		2304	2290		2291	2275		2221	2221	ν_3
A_1	ν_4	(2988)	(2988)	(2152)			1247	1282		1240	1215		1358	1379	ν_4
	ν_5	(1444)	(1447)	(1073)			752	763		808	863		1043		ν_5
S_2	ν_6	3068	3072	2308	2306	σ_ν	3031		A	3053		σ_x	3088		ν_6
	ν_7	950	944	758	780			2229			2233			2316	ν_7
A_2	ν_8	(3107)	(3107)	(2325)			1295			1308			946		ν_8
	ν_9	(949)	(949)	(678)			820			765			725		ν_9

Manneback and Verleysen.¹⁰¹⁷ Tchang,¹⁵³⁵ by correcting the potential function for the anharmonicity, has obtained results which fit experimental data more accurately.

In this table the letters S and A designate that the motion of the vibrating atoms is symmetrical or antisymmetrical, respectively, with reference to the center, and the subscripts 1 and 2 indicate that the vibrations are parallel or perpendicular. The letter π or σ indicates whether the motion is symmetrical or antisymmetrical with reference to the x or z axes. None of the vibrations designated by A are allowable in the Raman effect. The σ vibrations are permitted but are missing. The values given in parentheses are calculated and observed in the infrared absorption. Raman lines which may be classified as S or π are relatively strong and polarized. The types of vibration designated by ν_1 , ν_2 , etc. are only directly related in any two compounds in the case of ethylene and ethylene-d₄.

It has been shown¹⁰¹⁷ that many of the lines in the *cis*, *trans* or *asym* compounds represent an arithmetical mean between either two lines in ethylene or one line in ethylene and another in ethylene-d₄. Some of this is explained on the basis of a coupling between vibrations.

In the $\text{C}_2\text{H}_2\text{D}_2$ compounds the ν_1 vibration corresponding to $\text{C}=\text{C}$ represents a compromise between $\Delta\tilde{\nu}$ 1620 and 1514. In *cis*= $\text{C}_2\text{D}_2\text{H}_2$ the $\pi_\nu\nu_2$ oscillation ($\Delta\tilde{\nu}$ 3046) is approximately the mean of $\text{S}_1\nu_2$ ($\Delta\tilde{\nu}$ 3007) and $\text{A}_2\nu_8$ ($\Delta\tilde{\nu}$ 3107). Similarly $\text{S}_\nu\nu_3$ (2275) for the *trans* isomer represents the mean of $\text{S}_2\nu_6$ and $\text{S}_1\nu_2$, *i. e.*, $\frac{1}{2}$ (2308 + 2283) = 2795. A last example may be selected from the *asym* vibrations. The $\pi_x\nu_3$ corresponds to $\Delta\tilde{\nu}$ 2221 which is the mean of $\text{A}_1\nu_4$ and $\text{S}_1\nu_2$ or $\frac{1}{2}$ (2152 + 2283) = 2217. This is particularly interesting inasmuch as, for example, $\text{A}_1\nu_4$ is not observable in the Raman effect at all but only in infrared absorption. It is concluded by de Hemptinne that the anharmonicity correction for the S_1 group amounts to 2 per cent and for the S_2 group to 3 per cent.

In all these compounds four to six lines have been observed (between $\Delta\tilde{\nu}$ 2100 and 2500) that are unassignable at present. None of the com-

pounds investigated was entirely pure. The amount of exchange between H atoms and D atoms was determined by intensities.

Diolefins

As has been pointed out, the substitution of a hydrocarbon radical in the place of a hydrogen atom in ethylene causes an augmentation of the normal ethylenic shift from $\Delta\bar{\nu}$ 1620 to approximately 1642. In the diolefins the substitution is in a sense of the type $\text{RHC}=\text{CH}_2$, and consequently it is to be expected that there would be an augmentation in the ethylenic frequency as compared with ethylene itself. Otherwise it may be stated that the effect of this conjugation is negligible. There is only one ethylenic frequency in the diolefins and, with the possible exception of butadiene, this frequency falls in the same place as any other substituted ethylene. Bourguel²⁶⁵ and Piaux¹²³⁷ postulate that the effect of conjugation is to reduce the ethylenic frequency over what would be expected theoretically. There is a tendency in this direction, but the amount of reduction is generally less than the experimental error involved in the measurement of the ethylenic frequency.

Conjugation in ring structures, as exemplified by benzene, is a separate problem and will be reserved for future consideration.

However, one type of structure which appears in the aliphatic hydrocarbons and may appear in the cyclic compounds has, from the point of view of spectroscopy and chemistry in general, a decided interest. This is the structure found in the allenes and their derivatives. From an organic standpoint these compounds have the general structure $\text{RC}=\text{C}=\text{CR}'$. On first examination one rather expects a normal ethylenic linkage from a spectroscopic point of view. This is not in accordance with observations, although Linnett and Avery have noted 11 fundamental modes of vibration including $\Delta\bar{\nu}$ 1684 and 1956. In place of the expected intense line in the region of $\Delta\bar{\nu}$ 1640, one or two frequencies which are quite characteristic of these compounds, appear in the region of $\Delta\bar{\nu}$ 1080 to 1130. Allene, like carbon dioxide, is a linear molecule. The nature of the vibrations is such as to allow a coupling between the vibrating components in such a way that the usual ethylenic shift is split into two parts, one occurring at a lower frequency corresponding to the symmetrical vibration and another at a higher frequency corresponding to the asymmetrical or anti-symmetrical one. As the latter may appear only very weakly in the Raman effect it may not register. The result is that the characteristic frequency appears at a position corresponding to the lower component of this split frequency of vibration and has a value less than expected. It is true that a re-evaluation of the reduced mass from that usually taken between a $\text{C}=\text{C}$ linkage in the simple formula for calculating the force constant in

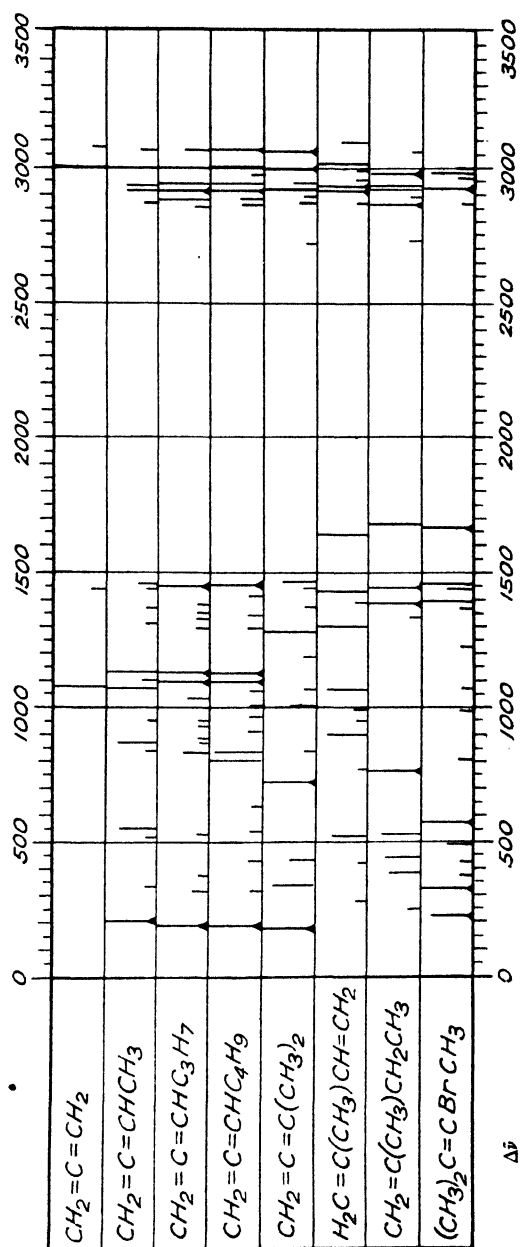


FIGURE 27A. The Raman Spectra of Some Allenes and Some Olefins (after Lespiau and Grédy).

any type of linkage will yield results which agree as a rough approximation in the inverse ratio of $\sqrt{2}$, and will consequently yield a calculable result reasonably comparable with that observed. It is felt, however, that this agreement is rather fortuitous and that the shift to a lower frequency in the case of allenes is more fundamental than a mere change in mass.

It may be mentioned also that ketene, according to Kopper,⁸⁹⁴ yields no normal ethylenic shift but a strong line at $\Delta\bar{\nu}$ 1130. Dimeric ketene, according to Angus, Leckie, le Fèvre and co-workers, exists primarily in the enol form: $\text{HO}-\text{C}=\text{CHCOCH}_2$. Kohlrausch and Skrabal (Raman Jubilee volume) have also investigated dimeric ketenes.

In any case the allenic compounds have well-defined shifts quite characteristic of their structures, and by this means any compound containing this type of linkage can be differentiated from other aliphatic compounds. These compounds have been investigated by Bourguet and Piaux,^{270, 271} by Piaux¹²³⁷ and by Kopper and Pongratz.⁸⁹⁶ In Figure 27A are given the Raman spectra of some of the allenes thus studied.

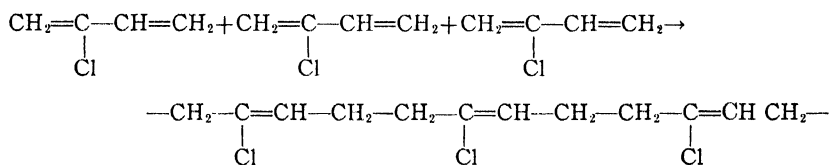
From these it can be noted that there is an apparent splitting of the single frequency occurring near $\Delta\bar{\nu}$ 1100 in the two completely symmetrical molecules, allene and ketene. This gives rise to a pair of strong lines in this region, probably due to the asymmetry of the molecule with reference to the position of the allenic structure. In the simple symmetric molecule these frequencies are degenerate.

The material presented thus far in the form of data and in the analyses of theoretical and experimental results is sufficient to demonstrate the practical utility of Raman effect research as well as its more academic applications. This practical aspect should be of interest to the chemical industries as a means of solving some of the problems which eternally confront them. This point is re-emphasized here because the general treatment in this book is from the standpoint of pure compounds. This does not preclude the investigation of hydrocarbon mixtures found in petroleum fractions, or the cracking of gasoline.^{730, 741} For example, the French Ministre de l'Air (Andant) has published the results of a number of such investigations. Numerous other applications such as the analysis of complex mixtures of naturally occurring terpenes will be indicated in due course. In applied biochemistry the constitution of amino acids, sugars, proteins and other compounds are naturally of interest and importance, and the utility of constitutional determinations is, of course, obvious to the organic chemical industry interested in synthesized products. The use of Raman spectra as a tool to study the mechanism of polymerization in the plastic field has already been mentioned.

However, for the sake of further illustration attention will be called here to work by Gehman and Osterhof⁵⁸⁴ on the Raman spectra of rubber,

balata and isoprene, and by Kubota on the spectra of chloroprene and polychloroprene. Balata and rubber both have an ethylenic shift at $\Delta\bar{\nu}$ 1670 although their spectra otherwise have some notable differences. Isoprene was found to yield $\Delta\bar{\nu}$ 1640 for the C=C shift and trimethylethylene $\Delta\bar{\nu}$ 1679. The spectrum from myrcene is nearly a superposition of the spectra of isoprene and trimethylethylene. The fact that no $\Delta\bar{\nu}$ 1640 is found in rubber indicates a chain length so long that the isoprene group cannot be detected. It is concluded from a comparison of the spectra of all these compounds that rubber consists of a long chain of isopentene units.

Kubota obtains practically the same spectra from chloroprene (liquid) as from polychloroprene (solid), the principal exception being a doubling of $\Delta\bar{\nu}$ 1628 (15), observed in the liquid, to $\Delta\bar{\nu}$ 1628 (15) and 1658 (3) in the solid. The latter frequency is not far removed from $\Delta\bar{\nu}$ 1670 obtained from 2-chloro-2-butene. If the polymerization mechanism was according to the scheme:



followed by a periodic interlinking of the chains thus formed, the spectrum of polychloroprene should differ appreciably from that of chloroprene and bear a considerable resemblance to that of 2-chloro-2-butene. This is not the case. It is concluded from the intensities of the Raman lines that polymerization proceeds linearly but not to a large extent. In the solid state, at least in the first stage, the amount of interpolymerization must be small.

Chapter 12

The Raman Spectra of Compounds Containing the Carbonyl Linkage

From the point of view of classic organic chemistry it might be more logical to discuss cyanogen compounds or the acetylenes at this point than to discuss the carbonyl compounds. Nevertheless, as observed from Raman spectra, the differences between triple-bonded and double-bonded compounds are much greater than the differences between the double-bonded compounds themselves. For this reason the carbonyl compounds will be considered here and the acetylenic type of linkage reserved for later discussion. The Raman spectra of the carbonyl type of linkage are very similar to those of double-linked carbon in the ethylenic compounds. The increased mass of the oxygen atom would be expected to cause a lowering of the frequency shift to a value less than that observed in the case of the ethylenic linkage. Experimentally, however, the minimum shift approaches the maximum value observed in the ethylenes, about $\Delta\tilde{\nu}$ 1666, and is always polarized. The maximum for the anhydrides is near $\Delta\tilde{\nu}$ 1800, which indicates that the force constant is somewhat greater in this type of compound than in the corresponding ethylenes.

While it is possible in specific instances to confuse the carbonyl frequency with a maximum ethylenic frequency, as a rule this causes no difficulty. Hence, like the ethylenic shift, this permits a delineation of structure which is more or less unique.

Acids

While the effect of the carbonyl group, as exemplified first by the acids, remains fairly constant compared with the behavior of the C—C linkage, there is, nevertheless, a variation in the magnitude of the shift as a function of substitution either on the carbon atom adjacent to the carbonyl group (α -position), or as a substitution directly onto the carbon atom which is connected to the double-bonded oxygen. As in the ethylenic shift, these displacements appear in a separate portion of the spectrum, and their modifications are directly connected with the type of substitution. These may be used to delineate the structure of molecules containing this type of grouping. The influence of such substitution on the carbonyl frequencies is indicated in Table 19.

It is apparent that the average carbonyl shift in the aliphatic acids is approximately $\Delta\bar{\nu}$ 1654. In butyric acid this is $\Delta\bar{\nu}$ 1654, in isobutyric acid $\Delta\bar{\nu}$ 1649, and in trimethylacetic acid $\Delta\bar{\nu}$ 1645. The effect of substituting halogen in the molecule to form the chloracetic acids has been studied by Cheng,³⁶³ Ghosh and Kär,⁵⁹⁹ Thatte and Ganesan,^{1542, 1544} Woodward¹⁷³¹ and Parthasarathy.¹²¹⁰ The effect of chlorine substitution is to augment

Table 19.—The Influence of Substitution on the Carbonyl Frequencies.

Substance	$\Delta\bar{\nu}$				
	H ₃ CCOX	RH ₂ CCOX	R ₂ HCCOX	R ₃ CCOX	C ₆ H ₅ COX
Acid, X = OH	1666	1652	1648	1644	1647
Methyl ester, X = OCH ₃	1736	1735	1732	1728	1720
Ethyl ester, X = OC ₂ H ₅	1736	1732	1728	1724	1721
Ketone, X = CH ₃	1710	1709	1709	1702	1677
Acid chloride, X = Cl	1798	1793	1788	1790	
Aldehyde, X = H	1715	1719	1719	1723	1689

considerably the magnitude of the carbonyl frequency and to decrease somewhat its intensity. It becomes a broad band from $\Delta\bar{\nu}$ 1675–1740 in the monosubstituted acids, and splits into two lines corresponding to $\Delta\bar{\nu}$ 1678 and 1740 in the disubstituted acids and 1682 and 1740 in the tri-substituted compounds. This splitting of frequencies into one or more components, as previously pointed out, may be due to a decrease in degeneracy but it may also be due to a decrease in hydrogen bonding.

Kohlrausch,⁸⁴⁷ Peyches¹²²⁷ and Gupta⁶⁷² have examined a number of acids and believe that a modification of the carbonyl group accounts for alterations in the carbonyl frequencies. Sannié and Poremski¹⁴⁰⁶ think that $\Delta\bar{\nu}$ 1650 is due to the carbonyl shift in associated molecules of the acids and that $\Delta\bar{\nu}$ 1730, which appears on dilution, can be assigned to the unassociated molecule. The association which gives rise to $\Delta\bar{\nu}$ 1650 is attributed to hydrogen bond formation between the hydroxyl radical of one acid and the carbonyl group of the other. This explanation was likewise used by Hibben,⁷³¹ as will be mentioned, to account for the behavior of oxalic acid. Edsall⁵¹⁵ likewise comes to the conclusion that the carbonyl frequencies in the lower fatty acids appearing near $\Delta\bar{\nu}$ 1650–1670 are attributable to the polymerized form of these molecules. This thesis is predicated on the observation that in aqueous solutions of these acids the carbonyl shift is altered to $\Delta\bar{\nu}$ 1720. This is partially substantiated by the shift at $\Delta\bar{\nu}$ 1740 appearing in the hydrochlorides of the amino acids which possess an R—COOH group. Formulas based on quadrivalent oxygen are proposed for associated acids by Chelintsev; and Vol'kenshtein states that if the association forces are less than 10,000 calories, the molecules can be regarded as unassociated, but if the association energy approaches that of a homopolar or a heteropolar linkage the product is intermediate between a chemical compound and a van der Waals complex. Koteswaram has

examined the spectrum of acetic acid in polar and non-polar solvents and concludes that the acid is highly polymerized, the degree of polymerization being affected by the temperature and by the ionization capacity of the solvent. Several lines besides the $\text{C}=\text{O}$ frequency, which is displaced from $\Delta\bar{\nu}$ 1673 to 1710, are affected by dilution.

There is not only a question of a modification of the carbonyl shift in solutions sufficiently concentrated so that a large portion of the acid present is un-ionized and polymerized, but also there is a question of the complete disappearance of this frequency on ionization in most cases. The alkali salts of these acids exhibit either no carbonyl frequencies or extremely weak ones. This behavior will be discussed in more detail under dicarboxylic acids.

The appearance of another line in the spectra of the completely ionized acids must next be considered. This line appears at $\Delta\bar{\nu}$ 1360 and is probably assignable to the carboxyl ion. Studies of alkali salts of formic acid by Venkateswaran¹⁶²⁶ indicate the presence of a $\text{C}-\text{H}$ linkage from the hydrogen shifts at $\Delta\bar{\nu}$ 1390, 2732 and 2834, thus eliminating the possibility of the presence of the isomeric dihydroxymethylene in any quantity. The $\Delta\bar{\nu}$ 1351 shift of the carboxyl ion is present in sodium formate but not in the spectra of either the acid or an aqueous solution of the acid. Therefore, in this region of the spectrum there exists for the formate ion 1351(6) and 1390(1); for the acid only $\Delta\bar{\nu}$ 1400(3) appears, the larger shifts being assigned to the $\text{C}-\text{H}$ bending frequency in both cases. Gupta⁶⁷² records a double carbonyl shift for pure formic acid, namely, $\Delta\bar{\nu}$ 1672(4) and 1724(2) which become $\Delta\bar{\nu}$ 1708(4) in a solution of the acid. The frequencies near $\Delta\bar{\nu}$ 1353–1375 are assigned to a vibration of the carboxyl ion. The non-existence of a hydroxyl group in the formate ion is further substantiated by Small and Wolfenden, who have determined the rate of deuterium substitution, which should be rapid in a hydroxyl group. These experiments indicate a very slow deuterium substitution. The recent work of Hafstadter on the infrared absorption of formic acid indicates a $\text{C}-\text{H}$ frequency extant in the pure acid which persists along with the frequency shifts attributed to the polymeric forms of formic acid in the gaseous stage. No discussion of formic acid would be complete without mentioning the shift $\Delta\bar{\nu}$ 175–200 which is extremely broad and is probably connected with a type of hindered rotation which, it will be seen, occurs in the spectrum of water.

In pure acetic acid $\text{C}-\text{H}$ frequencies have been ascribed to a doublet at approximately $\Delta\bar{\nu}$ 1365(1) and 1436(2). The acetate ion from sodium acetate is characterized by $\Delta\bar{\nu}$ 1347(2) and 1413(6), the first of these being attributed to the carboxyl ion and $\Delta\bar{\nu}$ 1413 to a degeneracy of the doublet $\Delta\bar{\nu}$ 1365–1436 in the acid into a singlet in the ion. Sidorova¹⁴²⁸ observes

that the $\Delta\bar{\nu}$ 895 shift splits into 884 and 904 in solid acetic acid, and that there are possibly two well-defined wings at $\Delta\bar{\nu}$ 49 and 119 in the solid.

A 50-per cent aqueous solution of acetic acid has approximately the same spectrum as the anhydrous acid with the exception of $\Delta\bar{\nu}$ 1670, which is shifted to $\Delta\bar{\nu}$ 1720. There is no evidence of any O—H vibration at $\Delta\bar{\nu}$ 3445 as reported by Bernstein.¹¹⁸ This is shown in Figure 28 which also indicates a shift at $\Delta\bar{\nu}$ 2721 not reported by others.

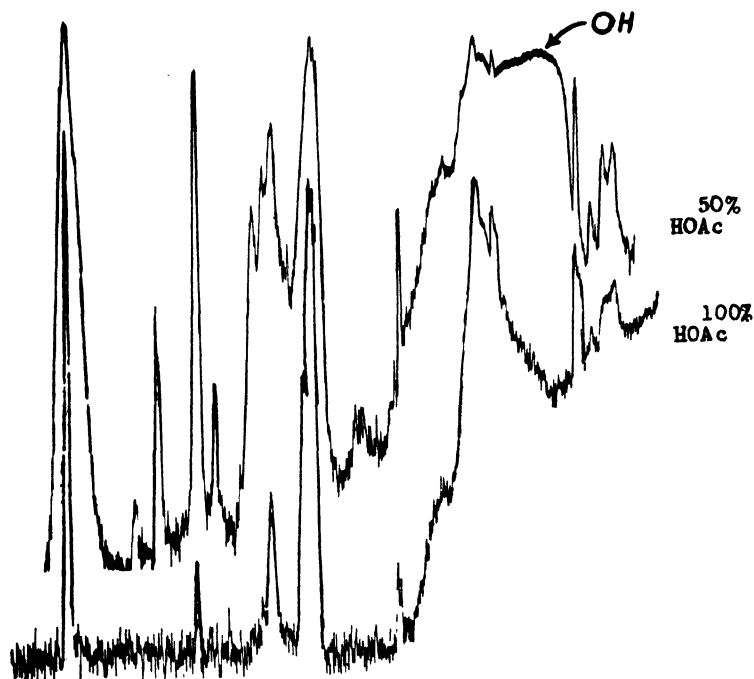


FIGURE 28. Microphotometer Tracings of the Raman Spectra of Anhydrous Acetic Acid and of an Aqueous Solution of Acetic Acid showing the Absence of the O—H Band in the $\Delta\bar{\nu}$ 3200-3600 Region.

Angus, Leckie and Wilson⁷⁰ have examined the spectrum of acetic acid, acetic acid-d and acetic-d₃ acid-d. The carbonyl frequency is decreased by only 30 wave numbers. The ordinary C—H vibrations are in the ratio of the square roots of the reduced masses. The symmetrical C—H vibration at $\Delta\bar{\nu}$ 2935 becomes, for example, $\Delta\bar{\nu}$ 2111 in the acetic-d₃ acid-d compound, but is unaltered in the acetic-d compound. In a similar fashion $\Delta\bar{\nu}$ 1431 and 1359, appearing in the pure acid, become $\Delta\bar{\nu}$ 1093 and 1025 respectively. The two strongest low frequencies in acetic acid $\Delta\bar{\nu}$ 623(3) and 898(6), as well as one or two other very faint lines, are

decreased to $\Delta\bar{\nu}$ 580 and 800 in the completely deuterium-substituted acids. The values for these two shifts in acetic acid-d are midway between these two extremes. These frequencies are due to the C—C vibrations and are more strongly influenced by this substitution than would normally be expected. These experiments, however, serve the purpose of indicating in an unequivocal fashion that the previous assignment of types of vibration in these compounds has been reasonably correct.

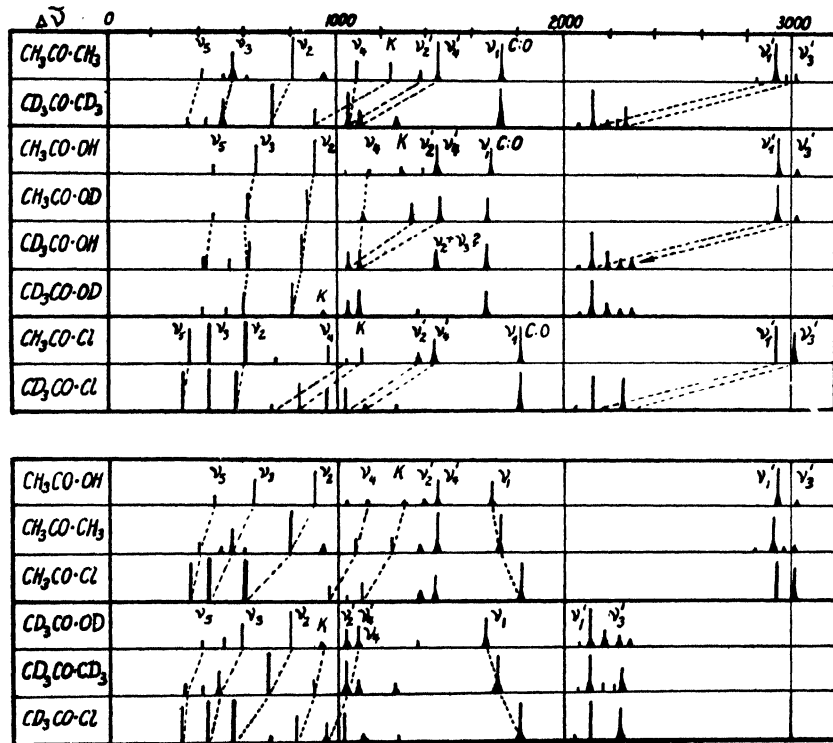


FIGURE 29. The Raman Spectra of Acetic Acid, Acetone and their Deuterium Derivatives (after Engler).

Engler⁵³² has also investigated acetic acid-d and acetic-d acid-d as well as a number of deuterium-substituted ketones. Some of the results obtained with both the acids and ketones are shown in Figure 29. The vibrations designated by ν_1 to ν_4 are hydrogen vibrations, and those by

ν_1 to ν_6 represent the oscillations of a molecule of the type $\begin{array}{c} \text{C} \\ | \\ \text{A} \\ / \quad \backslash \\ \text{B} \quad \text{B} \end{array}$ having

the symmetry D_{2v} in those cases where such a structure would represent an approximation to that of the compounds investigated. In Chapter 8, in the discussion of the Raman spectrum of methane, it was pointed out that the methyl group may be considered as having a pyramidal structure, in which case the order of the frequencies from low to high will be $\nu_2, \nu_4, \nu_1, \nu_3$, where the two parallel vibrations are represented by ν_1 and ν_2 . With the addition of primes, this is the designation used by Engler. The fundamental chain vibrations referred to above, for a molecule AB_2C , are six in number, ν_1, ν_2 and ν_3 representing the three symmetrical vibrations which yield three polarized Raman lines. The remaining three vibrations are antisymmetrical and the resulting Raman lines are depolarized.

In Figure 29 is shown not only the change in frequency caused by the introduction of deuterium but also the modifications of the principal lines on halogen or hydroxyl substitution.

Returning then to a consideration of the normal fatty acids as a group, it is to be noted that the shifts occurring in the $\Delta\bar{\nu}$ 1440 regions corresponding to the usual bending moment of the C—H linkage appear generally as a doublet frequency and occasionally as a triplet frequency throughout the whole series. The other types of carbon-to-hydrogen vibrations give rise to very strong lines. In acetic acid $\Delta\bar{\nu}$ 2937(19), 2986(1) and 3033(1) appear. For the remainder of the series there appear four or five fairly strong hydrogen lines.^{352, 618} Of these, 2756(2) in propionic acid becomes 2739 in butyric, 2730 in valeric and 2729 in caproic acid. The line occurring at $\Delta\bar{\nu}$ 2888(4) in propionic acid decreases slightly to 2875(9) in butyric acid, after which there is no subsequent reduction. The third frequency at 2921(6) in propionic acid decreases to 2912 in butyric, after which this likewise remains practically unaltered. The hydrogen shift at $\Delta\bar{\nu}$ 2944(12) for propionic acid becomes $\Delta\bar{\nu}$ 2935 in caproic and 2930 in pelargonic acid $\Delta\bar{\nu}$ 2986(8) similarly decreases with increased chain length until in caproic acid it is reduced to 2963. In other words, of the hydrogen frequencies, the lower and higher frequency groups decrease as the length of the chain is increased. The middle frequencies represented by a forty wave number spread are at first initially decreased and then remain fairly constant. All these changes are reported in Figure 30.

In the region between $\Delta\bar{\nu}$ 500 and 1000 there is at least one strong line which appears near $\Delta\bar{\nu}$ 900. This decreases regularly to $\Delta\bar{\nu}$ 736 on the substitution of methyl groups or ethyl groups on the carbon atom α to the carboxyl group. In pivalic acid (α, α -dimethylpropionic acid) there are two shifts, $\Delta\bar{\nu}$ 589(4) and 753(10), and in α, α -dimethyl-butyric acid $\Delta\bar{\nu}$ 575(5) and 736(8).

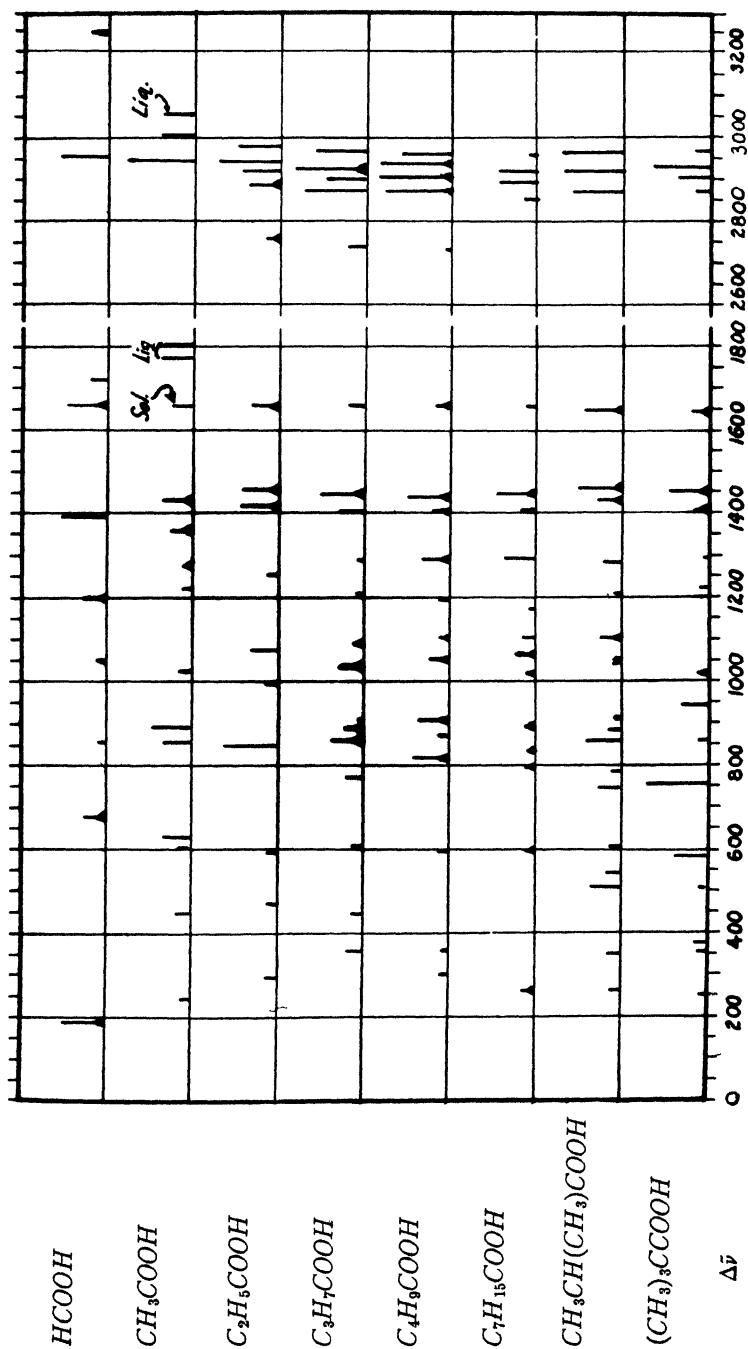


FIGURE 30. The Raman Spectra of Some Aliphatic Monobasic Acids.

Ketones

The carbonyl shift in the aliphatic ketones is considerably greater than that observed with the acids and slightly less than that with the aldehydes. The average displacement is at approximately $\Delta\bar{\nu}$ 1710 for the aliphatic derivatives. The constancy of this shift is usually greater than the accuracy of its measurement when both groups attached to the carbonyl carbon atom are hydrocarbon radicals. There seems to be a slight diminution from $\Delta\bar{\nu}$ 1710 to 1701 when increased centralization occurs in compounds of the type methyl *tert*-butyl ketone, that is when two or more alkyl groups are attached to one carbon atom. This diminution is considerably greater if the hydrocarbon radical is a phenyl group. In general, in compounds of the type $X-CO-R$, as has been illustrated in Table 19, the influence of substitution of the radical X is to increase the carbonyl shift in the following order: C_6H_5 , CH_3 , C_2H_5 , H , OR' and Cl where X represents any of these radicals. If R is replaced simultaneously the frequency will also increase in the order given.^{828, 860} The characteristic frequency of a series of aliphatic ketones is shown in Figure 31. Cheng and Lecomte³⁶⁹ have investigated the halogen derivatives of ketones.

Engler and Kohlrausch⁵³³ have studied a peculiar type of carbonyl compound, namely, carbon suboxide, C_3O_2 . As this is a linear compound the total number of possible vibrations is ten, of which three represent possible fundamental vibrations and are Raman active. More than this number were observed but several represent doubtful lines. Those whose existence is certain are $\Delta\bar{\nu}$ 586(3), 843(4) and 2200(2). In addition there are two faint lines at $\Delta\bar{\nu}$ 1114 and 1176, one of which may represent an overtone of $\Delta\bar{\nu}$ 586. The exact meaning of the $\Delta\bar{\nu}$ 2200 shift is not entirely clear if double-bond linkage is assumed. It is considered to be one of the fundamentals and may be ascribed to the vibration of the two end oxygen atoms against the adjacent carbon atoms. Thompson and Linnett¹⁵⁵⁷ maintain that the Raman spectrum of carbon suboxide indicates that the structure of molecule is a hybrid one in which the bonds behave nearly, but not entirely like, triple bonds and should be represented by $O\equiv C\equiv C\equiv C\equiv O$.

Aldehydes

The carbonyl frequencies in the aldehydes occur in the neighborhood of $\Delta\bar{\nu}$ 1720 and, like the ketones, remain relatively quite constant in the entire homologous series. Unlike the behavior of the ketones, there is a slight increase with hydrocarbon substitution on the α -carbon atom. On the other hand there is a notable decrease if the substituent is an aromatic radical rather than an aliphatic one. This effect, as in the case of the

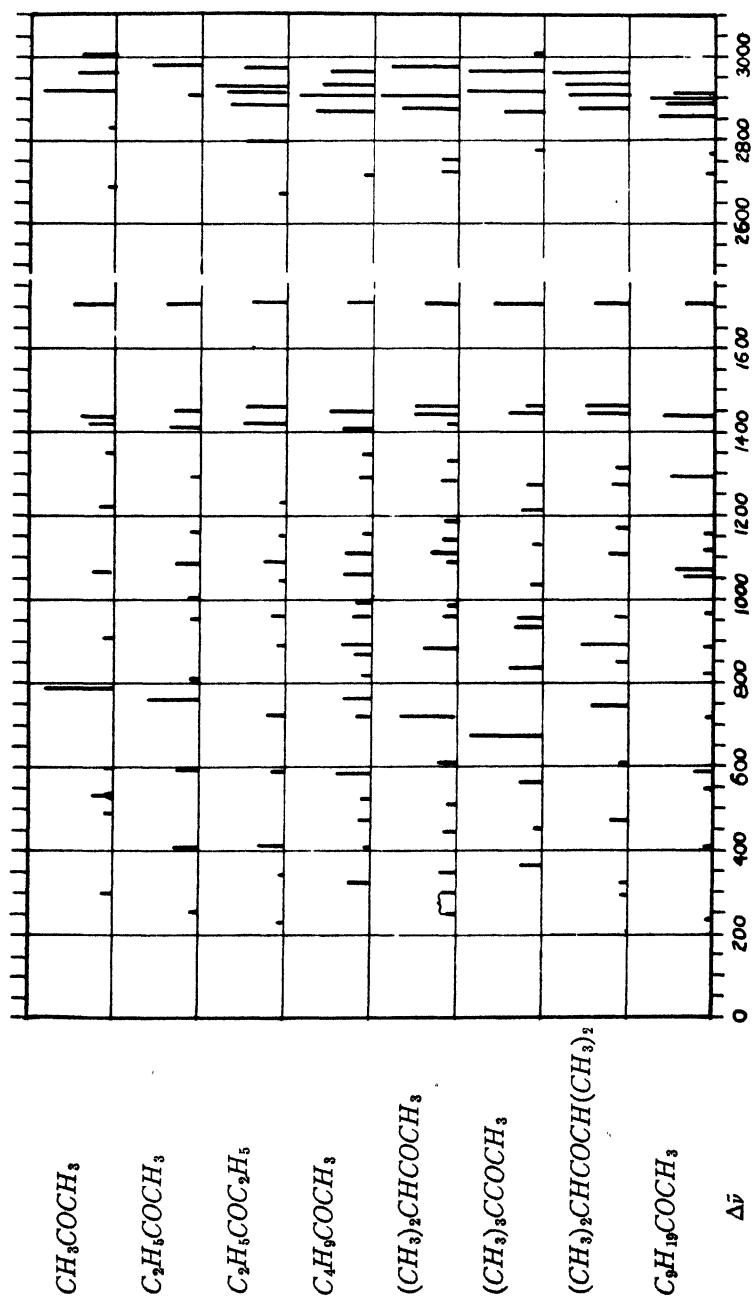


FIGURE 31. The Raman Spectra of Some Aliphatic Ketones.

ketones, is presumably attributable to conjugation of the ethylenic linkage with the carbonyl linkage. The aldehydes have been investigated in detail by Kohlrausch and Köppler.⁸⁴²

Formaldehyde, either in solutions containing a large excess of formaldehyde or in the gaseous state, apparently has a shift corresponding to $\Delta\bar{\nu}$ 1768. An interesting phenomenon was observed, however, by Hibben.⁷²⁷ If formaldehyde is dissolved in water so that the molar water concentration is in excess, no carbonyl frequency is obtainable. The spectrum has a relatively close similarity to that of glycol, pointing to the formation in solution of methylene glycol [$\text{CH}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2(\text{OH})_2$]. These results have been confirmed by Krishnamurti.⁹¹⁵ In paraformaldehyde Hibben⁷²⁷ has also noted that there is no carbonyl shift; this is similar to the result obtained with paraldehyde by Venkateswaran and Bhagavantam.¹⁶⁴² It was also supposed that paraldehyde, and possibly in this case paraformaldehyde, formed a ring structure consisting of three molecules bound together through the oxygen atoms, in consequence of which no normal carbonyl shift would be present. Such a frequency is also missing in chloral hydrate,¹²²⁴ but is present in chloral.^{431, 1224}

In addition to the carbonyl frequency characteristic of the aldehydes, $\Delta\bar{\nu}$ 510 and 1390 appear in the simpler aldehydes. These also seem to be fairly constant.

Table 20.—Isotopic Modification in Raman Shifts of Acetaldehyde and Acetaldehyde- d_4

Acetaldehyde $\Delta\bar{\nu}$	Acetaldehyde- d_4 $\Delta\bar{\nu}$
2966	<i>2128*</i>
2915	<i>2072</i>
2836	
2732	1692(?)
1715	1706
1428	<i>1024</i>
1392	1153
1352	1090
1111	
914	
887	762
512	422

*Italicized shifts refer to known isotopic changes.

Acetaldehyde- d_4 investigated by Wood¹⁷²² demonstrates that the frequency at 1428 in acetaldehyde is a C—H frequency. In the deuterio-compound the ratio of the C—D to the C—H frequencies is $1:\sqrt{2}$. The relationship between the frequencies obtainable from these two compounds is indicated in Table 20 where the italicized shifts have the correct ratios. The absence of some of the corresponding lines in the deuterium compounds is without significance and can probably be attributed to the

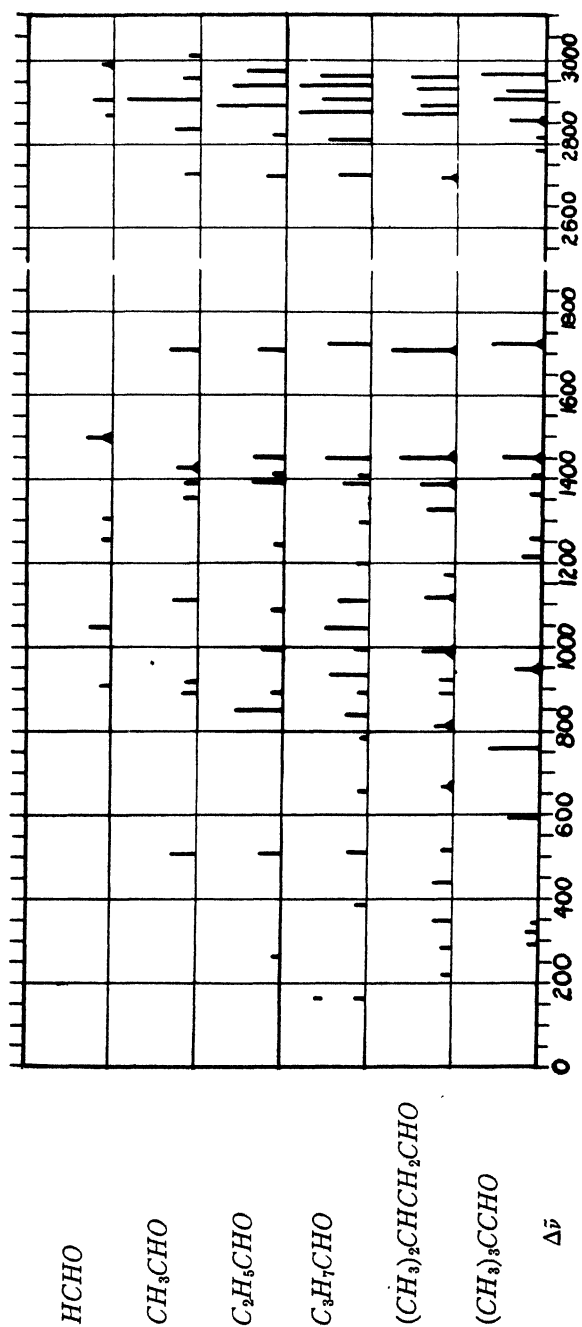


FIGURE 32. The Raman Spectra of Some Aliphatic Aldehydes.

failure of Wood to observe them. These experiments indicate that the shifts in the 1300 region are connected with the vibration of the heavier masses, probably oxygen, and are not related to hydrogen oscillations. The C—H shifts appear in the region between $\Delta\bar{\nu}$ 2700 and 3000 in their usual positions. The valence vibration generally occurs between 2915–2931. The presence of a double bond linkage adjacent to one of the hydrogens attached to a carbon atom does not have the effect on the $C \leftrightarrow H$ vibration that an ethylenic linkage has when similarly situated.

Characteristic spectra from a number of simpler aldehydes are shown in Figure 32.

Esters

The carbonyl frequency engendered by the esters is about midway on the scale of carbonyl shifts. The esters of formic acid have a frequency which occurs quite constantly at $\Delta\bar{\nu}$ 1718. This is independent of the length of the carbon chain occurring in the ester radical, for the methyl ester gives approximately the same shift as does the butyl ester. This is true of other esters. The substitution of a methyl group in place of the hydrogen atom in formic esters to yield the acetic ester causes an augmentation in the carbonyl shift of approximately 18 wave numbers. The substitution of hydrocarbon radicals of greater length than the CH_3 -group in the α -position to the carbon of the carbonyl group does not affect further the characteristic frequencies.

The modification in the carbonyl frequency as a function of substitution depends not only upon the nature of the substituent group but also upon its position in a given homologous series such as the esters. It has been mentioned that the effect of increasing the ester radical is more or less negligible. This is at least partly because the hydrocarbon component of the ester radical is in the β -position to the carbonyl carbon. In passing from formic to acetic ester there is quite an appreciable change since both the hydrogen on the one hand and the carbon of the methyl group on the other are in the α -position. This effect is still more pronounced after a chlorine atom is substituted for a methyl group, as in methyl chloroformate. This causes an augmentation in the frequency of the formic ester to $\Delta\bar{\nu}$ 1780, or an increase of approximately 40 wave numbers above that brought about by the methyl radical. If, however, the chlorine is attached to the α carbon atom, as in methyl chloroacetate, there is a slight increase to $\Delta\bar{\nu}$ 1748 as compared with 1740 for ethyl acetate. Further replacements of hydrogen by chlorine in the methyl group cause a still further increase so that finally, with the trichloroacetate esters, the shift has become $\Delta\bar{\nu}$ 1768. In other words, the substitution of the three chlorine atoms in the α -position has less influence

than one chlorine directly attached to the carbonyl carbon atom. The net effect of a bromine atom in ethyl monobromoacetate is virtually negligible. The increased mass would tend to reduce the frequency and at the same time the increase in the force constant would augment it. In either case there is an enhancement of the force constant, less for the bromine than for the chlorine, but becoming appreciable even in the α -position. Other esters have been investigated in considerable detail.^{363, 847, 1099, 1100, 1207, 1584} In Table 21 is given a summary of the effect of sub-

Table 21.—The Carbonyl Frequencies in Esters of the Type XCOOR.

Ester (XCOOR)	$\Delta\bar{\nu}$						
	X = H	X = Cl	X = CH ₃	X = CH ₂ Br	X = CH ₂ Cl	X = CHCl ₂	X = CCl ₃
1. R = CH ₃	1717	1780	1738	1740	1748	1755	1768
2. R = C ₂ H ₅	1715	1772	1736	1738	1747	1750	1763
3. R = C ₃ H ₇	1719	1775	1739	1736	1742	1749	1764
4. R = C ₄ H ₉	1718	1773	1737	1732	1739	1751	1765
5. R = C ₆ H ₁₁	1718	1774	1738		1744	1756	1769

stitution on the carbonyl frequencies in various esters taken from the data of Cheng.³⁶³ In these compounds not only is there an effect on the carbonyl frequency but, as is to be expected, there is a noticeable effect on those frequencies connected with the chain and characteristic vibrations. With compounds having the radical $\text{BrCH}_2\text{C}\begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix}$, these are $\Delta\bar{\nu}$

370, 550, 670, 710, 1740, 2960; with $\text{ClCH}_2\text{C}\begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix}$, $\Delta\bar{\nu}$ 410, 590, 700, 790,

1740, 2960; with $\text{Cl}_2\text{CHC}\begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix}$, 230, 420, 770, 1750, 3010, and with

$\text{Cl}_3\text{CC}\begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix}$, 200, 290, 430, 680, 830, 1765. In Figure 33 are given the

Raman spectra of some esters and salts of acetic acid taken from Cheng.³⁰⁷ The most characteristic point illustrated in this figure is the lack of lines corresponding to the carbonyl frequency in the salts. This may not be wholly absent but it is certainly diminished in intensity by a large factor. This has been noted by Kohlrausch,⁹¹⁵ Ghosh and Kär,⁵⁹⁹ Hibben⁷³¹ and Edsall.⁵¹⁹ This is not explicable on the same basis as a disappearance of the double bond frequency, as in the allenes. Generally this has been accounted for by a type of hydration, that is, the formation of a hydroxyl group or by hydrogen-bonding of the oxygen. Examples of the former are found in the case of formaldehyde and possibly in urea.^{915, 1203} The dibasic acids present a somewhat different problem which will be discussed shortly.

Anhydrides

Although some of those compounds will be considered as heterocyclic molecules, it is believed that they may be more properly treated in con-

nection with the carbonyl frequencies. The anhydrides have been only slightly investigated.^{70, 796, 865, 1210, 1544} Nevertheless, they present the unique property of having two carbonyl frequencies. One of the shifts occurring in the aliphatic anhydrides varies from $\Delta\tilde{\nu}$ 1745(2) to 1754(2), depending on the length of the chain, while the other at $\Delta\tilde{\nu}$ 1804 remains

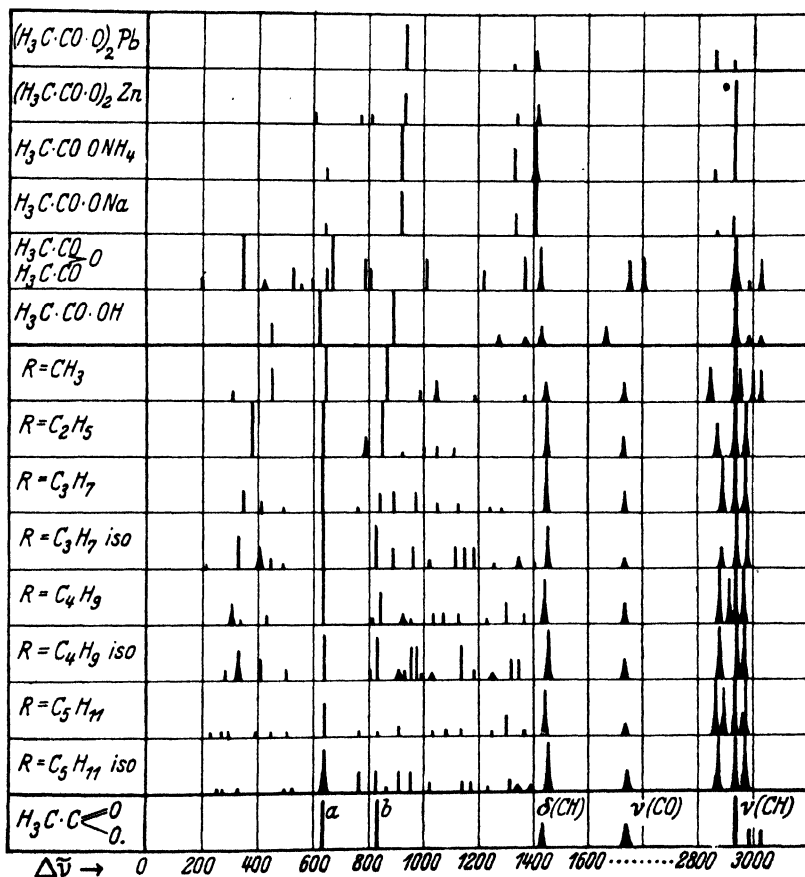


FIGURE 33. Raman Spectra of Acetic Acid and Some of its Salts and Esters (after Cheng).

fairly constant. Both of these shifts are higher than those observed with any other carbonyl compound with the exception of the halogen-substituted ketones and esters. At least one of the shifts, namely, $\Delta\tilde{\nu}$ 1804, is greater than that shown by any other type of compound containing a carbonyl group. Succinic, methylsuccinic, maleic and phthalic anhydrides yield $\Delta\tilde{\nu}$ 1775 and 1845. There may be some effect on carbonyl frequencies of

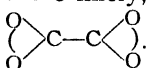
this type due to the ring structure, and it is to be noted that phthalide and furfural, containing a ring oxygen adjacent to the carbonyl group, possess only one carbonyl frequency shift. These compounds, however, lack the conjugation present in the succinic and other anhydrides just mentioned. It seems to be more probable that the doubling of the carbonyl frequency is due, from a chemical point of view, to the presence of two carbonyl groups in close juxtaposition. This is further substantiated by the study of polybasic acids. Angus, Leckie and Wilson, however, note but one frequency at $\Delta\bar{\nu}$ 1777 in acetic anhydride. They also report C—H frequencies at $\Delta\bar{\nu}$ 3118(1) and $\Delta\bar{\nu}$ 3201(0), which are somewhat exceptional. The dual behavior of ozonides and peroxides as anhydrides has been mentioned by Briner, Nemitz and Perrottet and by Soviet investigators.

Polybasic Acids and Their Derivatives

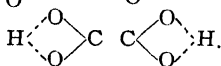
Some of the saturated polybasic acids which have been investigated are oxalic,^{427, 519, 673, 675, 731, 915, 1300} malonic,^{519, 599} succinic,⁸⁵⁵ tartaric,^{519, 1226} citric^{519, 1179} and tricarballic.⁵¹⁹ Dibasic acids have frequency shifts which may be strongly affected by their ionization and by other factors. In oxalic acid there are two frequency shifts in the aqueous solution and in the anhydrous material at $\Delta\bar{\nu}$ 1650 and 1750, one of which corresponds to the shift observed for a normal acid, while the other is nearer the ester or anhydride frequency. Hibben⁷³¹ has observed that there is apparently some suppression of the carbonyl frequencies in oxalic acid dihydrate. This is explained on the assumption that it has a chelate structure extending throughout long chains in the crystals, which breaks down in solution, permitting at least one of the carboxyl groups to function more normally. In alcoholic solution there is only one carbonyl shift $\Delta\bar{\nu}$ 1755, so that both carboxyl groups must behave identically in alcoholic solution. The increase in the force constant resulting from the increased carbonyl frequency is indicative of a stronger bond between carbon and oxygen in oxalic acid than in the other organic acids. It has been noted that a similar phenomenon results from the substitution of chlorine adjacent to the carboxyl group in the aliphatic acids, with a consequent increase in strength of these acids. Apparently the proximity of one carbonyl group to another increases the Raman frequency. This is notable in the case of pyruvic acid,^{425, 848} which has a shift $\Delta\bar{\nu}$ 1735(3), of malonic acid,⁶⁴⁸ $\Delta\bar{\nu}$ 1737, and of citric acid, $\Delta\bar{\nu}$ 1730. Anand,¹⁹ however, reports for the carbonyl shifts for crystalline oxalic acid $\Delta\bar{\nu}$ 1522, 1590 and 1658; for malonic acid $\Delta\bar{\nu}$ 1658; and for succinic acid $\Delta\bar{\nu}$ 1654.

Gupta^{673, 675, 677} observes only one band in the saturated solutions of the salts of oxalic acid at $\Delta\bar{\nu}$ 1600. There is likewise the appearance of $\Delta\bar{\nu}$ 1480. In view of the hypothesis that the $\Delta\bar{\nu}$ 1740 shift only appears in

unpolymerized, un-ionized molecules, it is presumable that its absence in oxalic salts indicates either a polymerization of the molecules or, as is more likely, an ionization. Gupta ⁶⁷³ depicts the oxalate ion in the form



The anhydrous acid would have the following structure:



On dissolving in water the molecule undergoes a

marked change in structure and the $\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix} \text{H}$ group is converted to the

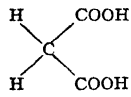
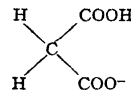
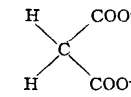
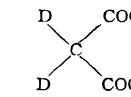
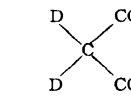
more normal $\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{OH} \end{smallmatrix}$ group, or $\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ in the ionized form. Hen-

dricks, however, from an x-ray analysis of anhydrous oxalic acid, concludes that there is a continuous structure set up in the crystal by means of the hydrogen bonding of the hydroxyl hydrogen of each acid with the carbonyl oxygen of the other. The potassium aluminum and potassium titanium oxalate complexes both show two carboxyl frequencies in contradistinction to diethyl oxalate, which shows only one. C. S. Rao ¹³⁰⁰ attributes $\Delta\bar{\nu}$ 1430 (probably correctly nearer to $\Delta\bar{\nu}$ 1470) observed in oxalic acid as due to the hydroxyl group oscillation. A shift, $\Delta\bar{\nu}$ 1450, is present in all the alcohols, but is more properly ascribed to the bending moment of the hydrogen. This is not a possible allocation of this frequency with oxalic acid, since no C—H group is present. Nevertheless, there is no other evidence in support of $\Delta\bar{\nu}$ 1430 as a hydroxyl vibration. The salts of the acid also show a frequency in this region and there is no indication of an $\text{O} \leftrightarrow \text{H}$ vibration in the anhydrous acid. This is similar to the behavior of acetic acid which likewise apparently possesses no such frequency. The $\Delta\bar{\nu}$ 850 and 480 observed are due to the linear chain and bending oscillations, respectively. Kohlrausch and Sabathy (Raman Jubilee volume) have added to the knowledge of dicarboxylic esters as a result of their studies of the ester derivatives of cyclobutane.

Edsall ⁵¹⁹ has investigated the effect of ionization in numerous dicarboxylic acids and their salts. In two cases, that of malonic acid and malonic- d_2 acid- d_2 , the steps in ionization have been studied in great detail. In other cases only the undissociated acids and their fully ionized salts have been examined. The results are compatible with the observations made on the fatty acids and indicate certain specific changes which accompany ionization of the carboxyl group. These results show that in the case of malonic acid the shift at $\Delta\bar{\nu}$ 1738 in the undissociated acid is decreased to $\Delta\bar{\nu}$ 1730 in the monosubstituted derivatives of the acid salt, and is greatly reduced in intensity. On disubstitution by alkali atoms there is no frequency at all in this region. This disappearance of the carbonyl frequency on ionization is characteristic of all the 26 carboxylic acids investigated. (This assumes that $\Delta\bar{\nu}$ 1587(1) is not of great impor-

tance.) New strong lines near $\Delta\bar{\nu}$ 1400 appear on ionization: one at $\Delta\bar{\nu}$ 1372 accompanies the first step of ionization and an additional one appears at $\Delta\bar{\nu}$ 1439 in the doubly charged ion. These are relatively unaffected by deuterium substitution. (Compare with un-ionized acetic acid which has $\Delta\bar{\nu}$ 1365–1436 doublet due to C—H; also with acetate ion, which has $\Delta\bar{\nu}$ 1347 for COO^- and 1413 for C—H). The line which occurs at $\Delta\bar{\nu}$ 1412, which may presumably be due to a deformation frequency of C—H, remains little changed in either position or intensity on ionization but is greatly affected by deuterium substitution. In spite of some dissimilarity between $\Delta\bar{\nu}$ 1372 and 1439 in disodium malonate and the corresponding vibration in sodium acetate at $\Delta\bar{\nu}$ 1347, these malonate lines are also due

Table 22.—The Raman Shifts of Malonic Acid and its Deuterium Derivatives.

(1)	(2)	(3)	(4)	(5)
				
427(4b)* 590(2b) 660(2b) 773(4b) 919(8b) 1031(0b) 1181(2b) 1308(0) 1417(4b) 1738(8b) 2956(6) 3003(3)	434(5) 586(2b) 664(3b) 802(2b) 923(8vb) 1193(1vb) 1278(4) 1372(5) 1408(5b) 1639(0vb)[H ₂ O?] 1730(2b) 2943(6) 2987(1)	427(3b) 590(3b) 698(1b) 828(3b) 935(6) 956(3) 1181(3) 1260(2b) 1361(6) 1413(6) 1439(6) 1587(1vb) 2947(6b) 2984(2b)	412(3) 538(4b) 607(1) 733(3) 790(4) 845(3) 940(0) 1106(4) 1360(1) 1050(4) 1209(4b)[D ₂ O?] 1719(7b) 2159(5) 2258(3)	414(1b) 573 ± 35(1b) 654(4) 810(2) 873(3) 910(2) 940(1) 1106(1) 1367(4) 1054(4) 1427(7) 1573(2b) 1228(4vb)[D ₂ O?] 2153(5) 2238(3)

*b stands for "broad"

vb stands for "very broad"

to the COO^- groups. There is also a weak line at $\Delta\bar{\nu}$ 1587 in the di-ion not visible in either of the other spectra. The other frequencies between $\Delta\bar{\nu}$ 430 and 600 remain unaffected by ionization as they are primarily deformation vibrations of the C—C—C chain. The line at $\Delta\bar{\nu}$ 660 is unaffected by the first step in ionization but is shifted upward to $\Delta\bar{\nu}$ 698 in the di-ion. The strong line at $\Delta\bar{\nu}$ 773 in undissociated acid is displaced by a large amount in the mono and di-ion, namely $\Delta\bar{\nu}$ 802 and 828 respectively. A similar increase occurs in $\Delta\bar{\nu}$ 919 of the undissociated acid. These results are indicated by Edsall and other workers in this field, as is illustrated in Tables 22 and 23. It will be seen that, in general, deuterium substitution changes the hydrogen frequencies in a manner similar to the modifications which took place in acetic acid.

According to Peyçhes,¹²²⁶ but not according to Nisi,¹¹⁷⁹ the salts of tartaric acid give a frequency shift $\Delta\bar{\nu}$ 1720 or 1660 depending on the mass of the anion. The presence of the carbonyl frequency in these salts is in

Table 23.—The Raman Shifts of Some Polycarboxylic Acids

		(1)	(2)	(3)	(4)	(5)
1. Oxalic Acid	$R \cdot (\text{COOH})_2^-$	1310(0)	1460($\frac{1}{2}$)		1645(2)	1750(3)
	$R \cdot (\text{COO})_2^{--}$	1311(4)	*1457(4)		*1580(1b)	
			*1489(7)		1647(2vb)	
2. Malonic Acid	$R \cdot (\text{COOH})_2$		1417(4b)			1738(8vb)
	$R \cdot \text{COOH}$	*1372(5)	1408(5b)			1730(2b)
	$\cdot (\text{COO})^-$					
3. Malonic-d ₂	$R \cdot (\text{COO})_2^-$	*1361(6)	1413(6)	*1439(6)	*1587(1vb)	
Acid-d ₂	$R \cdot (\text{COOD})_2$	1360(1)				1719(7b)
	$R \cdot (\text{COO})_2^{--}$	*1367(4b)		*1427(7)	*1573(2b)	
4. Succinic Acid	$R \cdot (\text{COOH})_2$	1339(0)	1409(3)		1637(3b)	1702(3)
	$R \cdot (\text{COO})_2^{--}$	*1330(3)	*1410(6)		*1555(3b)	
					1640(3b)	
5. Crotonic Acid	$R \cdot \text{COOH}$	1302(6)	1383(3)	1451(4)	1658(5)	1700(2)
	$R \cdot \text{COO}^-$	1297(5)	*1396(4vb)	1450(4)	1661(7b)	
6. Maleic Acid	$R \cdot (\text{COOH})_2$	1325(1b)	1390(1vb)		1654(6b)	1725(6vb)
	$R \cdot (\text{COO})_2^{--}$	1306(2)	*1400(6)		*1570(1vb)	
			*1434(2)		1647(6)	
7. <i>d</i> -Tartaric Acid	$R \cdot (\text{COOH})_2$		1413(1)	1442(2)		1740(5b)
	$R \cdot (\text{COO})_2^{--}$	*1310(2b)	*1418(6b)		*1617(1vb)	
		*1370(5b)				
8. <i>l</i> -Aspartic Acid	$R \cdot (\text{COOH})_2$	1376($\frac{1}{2}$)	1418(1)		1634($\frac{1}{2}$)	1743(4vb)
	$R \cdot (\text{COO})_2^{--}$	1330(1)	*1411(5b)		1620 = 50(1vb)	
		*1355(2)				
9. <i>d</i> -Glutamic	$R \cdot (\text{COOH})_2$	1347($\frac{1}{2}$)	1433(3)		1649($\frac{1}{2}$ vb)	1736(4vb)
	$R \cdot (\text{COO})_2^-$	*1345(2b)	*1410(4b)		*1625(2vb)	
10. Tricarballic	$R \cdot (\text{COOH})_3$		1420(5b)			1724(6b)
	$R \cdot (\text{COO})_3^{--}$	*1333(3b)	*1419(8b)		*1571(1b)	
11. Citric Acid	$R \cdot (\text{COOH})_3$		1403(3)	1438(2)		1731(6b)
	$R \cdot (\text{COO})_3^{--}$	*1302(0)	*1415(8b)		*1580($\frac{1}{2}$ b)	
12. Lactic Acid	$R \cdot \text{COOH}$	1381(1)	1446(3)			1710(3)
	$R \cdot \text{COO}^-$	1380(1)	*1411(5)		*1605–30(3)	
13. Glycolic Acid	$R \cdot \text{COOH}$	1372(1b)	1449(5)			1733(5b)
	$R \cdot \text{COO}^-$	1355(2b)	*1434(5b)		*1596(3b)	
					1632(3b)	
14. Sarcosine	$R \cdot \text{COOH}$	1284(1)	1429(2)	1464(3)	1622($\frac{1}{2}$ vb)	1732(1b)
	$R \cdot \text{COO}^-$	*1320(3b)	*1408(5b)	1468(4)	1633(2vb)	
15. Betaine	$R \cdot \text{COOH}$	1337($\frac{1}{2}$)	1419($\frac{1}{2}$)	1453(4)		1751(1b)
	$R \cdot \text{COO}^-$	*1335(2)	*1403(2)	1453(2)	1638(0b)	
16. Di-Methyl Phenyl Betaine	$R \cdot \text{COOH}$	1327(0b)		1468(3b)		1750(0vb)
	$R \cdot \text{COO}^-$	*1330(3b)	*1404(3b)	1465(3b)		
17. β -Alanine	$R \cdot \text{COOH}$	1328(2b)	1413(3b)	1472(1b)	1630(1vb)	1730(4b)
	$R \cdot \text{COO}^-$	1338(1)	*1410(5b)	1471($\frac{1}{2}$)	1630(1vb)	
18. β -Amino- <i>n</i> -Butyric Acid	$R \cdot \text{COOH}$	1380(2b)	1419(2)	1461(4)	1637(2vb)	1726(4vb)
	$R \cdot \text{COO}^-$	1366($\frac{1}{2}$)	*1408(7b)	1457(3)	1641(1vb)	

*Lines marked with an asterisk appear to be closely associated with an ionized carboxyl group.

contradistinction to the lack of this frequency in salts of the dibasic acids, oxalic acid⁷⁸¹ and malonic acid,⁵⁹⁹ already mentioned.

To review briefly, then, the status of the carbonyl shifts in the fatty and dibasic acids, it is clear that the shift normally occurring in the liquid

acids near $\Delta\bar{\nu}$ 1640 is increased to approximately $\Delta\bar{\nu}$ 1730 in aqueous solution. This is not a question of ionization because the solutions are too concentrated to be greatly ionized. Some acids, such as formic and oxalic, exhibit both these shifts simultaneously as the pure acids. In aqueous solution the $\Delta\bar{\nu}$ 1670 shift of formic acid is absent, but oxalic acid possesses both $\Delta\bar{\nu}$ 1650 and 1750 in aqueous solution. In alcoholic solution of the acid there remains only $\Delta\bar{\nu}$ 1750. These changes have been designated as depolymerization of the acid molecules without marked change in ionization. Ionization itself produces further changes in the acid molecule. These are the appearance of one or more frequencies near $\Delta\bar{\nu}$ 1350, 1370 or 1430 and the virtual disappearance or modification of the carbonyl frequencies at $\Delta\bar{\nu}$ 1720 or 1640. There is an appearance of a new line in the carboxyl ions near $\Delta\bar{\nu}$ 1580. This is not affected by deuterium substitution and is strongly depolarized according to Edsall.⁵¹⁹ The $\Delta\bar{\nu}$ 1720 shift, on the other hand, in malonic acid is polarized.

To explain these changes it has been postulated that ionization of the carboxyl group enhances the symmetry of this group, and that resonance between the two oxygen atoms, which is only partial in the un-ionized carbonyl group, presumably becomes more complete when the group is ionized. The ionized $\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ group, according to Edsall, is thus

intimately related to the structure of the nitro group $\text{N} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$. This suggestion is predicated on some measurements by Cabannes and Rousset²⁸⁵ on nitrobenzene and it rests on a somewhat ephemeral basis in view of the rather extensive measurements on other nitro-compounds not involving a conjugate linkage which yield frequencies more nearly $\Delta\bar{\nu}$ 1640 and are depicted by $-\text{N} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$. Furthermore the ionized carboxyl group should

be more analogous to the nitrite ion, which has no Raman shift corresponding to the usual double-bond frequency, but does have a wide line appearing at $\Delta\bar{\nu}$ 1337. Gupta⁶⁷² believes in a modified view of Hantzsch for the

$\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix} \text{H}$ structure when ionization is difficult, while Sidgwick postulates

$$-\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O}^- \end{smallmatrix}$$

Regardless of the quantity of careful work done thus far on the structure of the carboxyl ion, the problem is not yet solved. Edsall⁵¹⁹ has investigated *d*-tartaric and *meso*-tartaric acid. These two substances, as is to be expected, are extremely similar in type, but show definite differences in details which are well beyond the limits of experimental error in the determination of the frequency shifts. These differences are particu-

larly marked with respect to the lines near $\Delta\tilde{\nu}$ 1000. The mutual orientation of the hydrogen, hydroxyl and carbonyl groups attached to the two separate carbon atoms in these acids must inevitably give rise to differences in the internal fields of force which consequently must alter the frequencies corresponding to these specific modes of molecular vibration. This is similar to Hibben's observations with the sugars.

Unsaturated Carbonyl Compounds

The unsaturated carbonyl compounds, such as crotonyl chloride, have two strong shifts $\Delta\tilde{\nu}$ 1744 and 1761—a considerable reduction over the saturated acyl halide carbonyl shifts. The same diminution is also present in ethylideneacetone,⁸⁶⁰ which has $\Delta\tilde{\nu}$ 1668 for the carbonyl frequency; phorone has 1668. Apparently the conjugation of the carbonyl group with the ethylenic group in unsaturated compounds causes a reduction in the carbonyl frequencies of roughly forty wave numbers.

A few unsaturated aldehydes have been investigated. Here, likewise, there is a very marked lowering of the carbonyl frequency. This has been noted in 2-methyl-2-penten-1-al by Grédy⁶⁵² and in crotonaldehyde by Hibben.⁷²⁸ In both cases the shift was $\Delta\tilde{\nu}$ 1689. However, if the ethylenic double bond is sufficiently removed from the carbonyl group there is no longer any interaction between them, and the carbonyl frequency becomes normal, as in the case of citronellal,²²⁶ where the shift is 1719, and in undecylenaldehyde, where it is $\Delta\tilde{\nu}$ 1721, as observed by Bonino and Manzoni-Ansidei.²³⁰

The unsaturated acids are more or less characterized by the absence of a carbonyl shift. This is easily explicable for the following reasons. The acids have the lowest carbonyl frequency of all the compounds containing this group. Its normal position is from $\Delta\tilde{\nu}$ 1644 to 1666. If there is a reduction in this normal carbonyl frequency as a result of the interaction between it and the ethylenic bond, the net effect is one of superposition of the carbonyl frequency on the ethylenic one. Edsall⁵¹⁹ has observed, however, both the carbonyl and ethylenic shifts in aqueous solutions of crotonic and maleic acids as indicated in Table 23.

The explanation of this observation is probably to be found in terms of an effect previously observed by him, namely, the increase of the carbonyl frequency by about fifty wave numbers, which occurs when these acids are dissolved in water. Consequently in aqueous solution there is a greater separation of the ethylene and carbonyl frequencies. It is to be noted that on the average there is only a very slight effect on the ethylenic frequency, as compared with the variations in the carbonyl frequency, as a result of the inter-molecular hydrogen bonding. Nevertheless the solid dibasic acids like fumaric may possibly show a shift corresponding to the

carbonyl group in the region of $\Delta\bar{\nu}$ 1650.⁷²⁸ The esters of saturated dibasic acids^{429, 1203} yield a value $\Delta\bar{\nu}$ 1742 which is slightly higher than that observed for the esters of monobasic acids. The unsaturated esters^{438, 550, 658, 860} yield $\Delta\bar{\nu}$ 1725, on the average, which is some 20 wave numbers less than the equivalent saturated compounds. Hibben⁷³⁵ has observed that the ratio of the intensities of the ethylenic to carbonyl shifts is reversed as a result of *cis-trans* isomerism in these unsaturated compounds.

Keto-Enol Tautomerism

The demonstration of keto-enol tautomerism by means of the Raman effect was one of its earliest applications. A number of the acetoacetates have been investigated by Milone,¹¹⁰⁰ Dadiou and Kohlrausch,⁴²² Kohlrausch and Pongratz,^{848, 852, 853} and Pal and Sen Gupta.¹²⁰³ The last-named authors early pointed out the presence of two frequencies, $\Delta\bar{\nu}$ 1656 and 1750, in the ethyl acetoacetates. On re-evaluation, these are more nearly $\Delta\bar{\nu}$ 1632 and 1725. Methyl acetoacetate yields $\Delta\bar{\nu}$ 1626 and 1737; methyl methylacetoacetate yields $\Delta\bar{\nu}$ 1618, 1714, and 1734. Methyl dimethylacetoacetate shows no ethylenic shift, but yields $\Delta\bar{\nu}$ 1709 and 1738 as a doublet carbonyl frequency.⁸⁵² Methyl and ethyl pyruvate have the shift $\Delta\bar{\nu}$ 1735. These shifts are in all cases relatively strong. It may be seen immediately that only those compounds which can exist in an enolic form show evidence of the ethylenic linkage. Since the possibility of a migrating hydrogen ceases to exist when it is substituted by a methyl group, there is no longer any evidence of an ethylenic linkage in the disubstituted compounds. These shifts are illustrated in Figure 34.⁵⁴

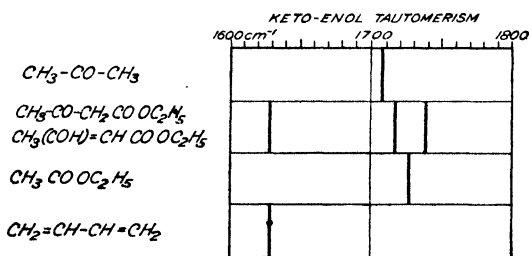
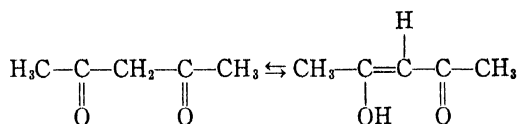


FIGURE 34. Raman Shifts of the Keto and Enol Forms of Ethyl Acetoacetate as Compared with those of Similar Compounds (after Andrews).

The possible tautomerism of β -aminocrotonic esters has been discussed by Kohlrausch and Pongratz.⁸⁵² The possibility of another type of keto-enol isomerism exists in aldol, which Hibben⁷²⁸ showed has both a reduced carbonyl frequency and an ethylenic shift similar to crotonaldehyde. Crotonaldehyde, however, was not present as an impurity.

Hayashi⁷⁰⁴ has investigated the Raman spectra from diacetyl, acetylacetone and acetonylacetone. He observed two shifts for diacetyl, $\Delta\tilde{\nu}$ 1677 and 2056, in the double-bond region. It is suggested that there is a type of tautomerism with these compounds not involving the migration of a hydrogen atom. These results are not compatible with those of Kohlrausch and Pongratz,⁸⁵² who obtained $\Delta\tilde{\nu}$ 1725(2) for diacetyl. Hayashi pointed out, in conformity with the well-known chemical evidence, that acetylacetone is tautomeric in nature. With this compound were observed $\Delta\tilde{\nu}$ 1600 attributed to C=C, $\Delta\tilde{\nu}$ 1859 for the C=O, and two frequencies, $\Delta\tilde{\nu}$ 3467 and 3563. The frequency shift in the region of $\Delta\tilde{\nu}$ 3500 is ascribed to the O—H shift. The frequency shift $\Delta\tilde{\nu}$ 1600(8) is confirmed by Kohlrausch and Pongratz,⁸⁵³ who observed in addition $\Delta\tilde{\nu}$ 1655(2) and 1723. These frequencies could be at least partially accounted for by the equilibrium between two tautomers:



This is partially substantiated by the fact that dimethylacetylacetone yields simply $\Delta\tilde{\nu}$ 1710 in much the same fashion as was observed for methyl dimethylacetoacetate. The results indicate a preponderance of the enol form in acetylacetone.

Chapter 13

The Raman Effect of the Acetylenes

As a rough approximation, calculation of the force constant, as a measure of the force exerted between the two triply-bonded carbon atoms in acetylene, gives a value which is nearly three times that calculated for the singly-bonded carbon atoms. Acetylene itself is something of an exception. The frequency value in this case is $\Delta\bar{\nu}$ 1960(5). The carbon-to-hydrogen frequency as it appears in acetylene is likewise augmented by the effect of the triple bond appearing near $\Delta\bar{\nu}$ 3320. This is one of the highest values observed in this type of linkage with the exceptions of $O \leftrightarrow H$ and $N \leftrightarrow H$ vibrations.

In addition to these frequencies Bhagavantam and A. V. Rao^{171, 172} have observed in acetylene, $\Delta\bar{\nu}$ 589 and 646, which are interpreted as maxima of the unresolved O, P, R and S branches of the totally symmetrical deformation vibration. They are of the opinion that there is no necessity for assuming a bent structure for this molecule.

Glockler and Renfrew⁶¹¹ observed in liquid acetylene $\Delta\bar{\nu}$ 560, 625, 636, 1259, 1934, 1961, and 3341. The shift at $\Delta\bar{\nu}$ 1259 is an overtone of the mean of the $\Delta\bar{\nu}$ 625–636 doublet. The first line of the pair of shifts at $\Delta\bar{\nu}$ 1934 and 1961 is attributed to the symmetrical oscillation in $HC^{13}\equiv C^{12}H$.

In a linear molecule of the acetylene type the maximum possible number of shifts is $3n-5$, or 7. However, Placzek¹²⁴⁶ has pointed out that this expected maximum number is decreased if the molecule has symmetry. Consequently in acetylene the total number of vibrations, both infrared and Raman active, is five, since two of the seven possible ones are doubly degenerate. These vibrations are indicated in Chapter 5. There are three Raman active vibrations: ν_1 , the $C\equiv C$ valence vibration, ν_2 , the $H-C\equiv$ valence vibration $\Delta\bar{\nu}$ 3341(P), and the vibrations of the carbon and hydrogen atoms perpendicular to the axis of the molecule, these last vibrations being out of phase with each other. This is ν_3 whose mean value is $\Delta\bar{\nu}$ 630(D). The two oscillations active only in the infrared are ν_3 at $\Delta\bar{\nu}$ 3228 and ν_4 , a deformation vibration, at 730. This leaves $\Delta\bar{\nu}$ 560 without a clear-cut explanation.

Glockler and Davis⁶⁰³ and Glockler and Morrell⁶⁰⁷ have obtained $\Delta\bar{\nu}$ 1762 and 2700 for $DC\equiv CD$, as compared with $\Delta\bar{\nu}$ 1975 and 3374 in

$\text{HC}\equiv\text{CH}$. In this case, assuming a value for k of 15.05×10^5 dynes cm^{-1} , calculated by means of the harmonic formula,

$$\Delta\bar{\nu} = 4.125\sqrt{\frac{k}{\bar{\mu}}}$$

for ordinary acetylene linkage, this leads to $\Delta\bar{\nu}$ 1901 as the expected acetylenic frequency, taking into consideration mass changes only. This does not agree with the observed result. Sutherland,¹⁵²⁴ Morino¹¹³² and Glockler and Morrell⁶⁰⁷ have made other calculations, based on somewhat different equations, which result in reasonable agreement.

It has been noted for ethylene that the substitution of a hydrocarbon radical augments the characteristic ethylenic frequency by an appreciable amount, namely, some 25 wave numbers. While this increase in terms of wave numbers is not exceptionally large, in terms of significant alteration of the ethylenic frequency as a function of substitution it constitutes a notable change. The acetylenes, like ethylene, show a considerable increase as a result of the substitution of a hydrocarbon radical in place of a hydrogen atom in acetylene. Here, however, the increase amounts to 160 wave numbers instead of 25. In other words, the triple bond is more sensitive to the effect of substitution than is the double bond. This is substantiated by the effects of other substitutions analyzed by the same procedure as that employed with ethylene. If one hydrogen is replaced, the 1960 frequency is augmented to $\Delta\bar{\nu}$ 2118. This would apparently indicate a slight increase in the force binding carbon atoms in the mono-substituted acetylene, as compared with the acetylene itself.

The exaltation of the acetylenic frequency (see Figure 12, Chapter 5) as a function of monosubstitution becomes still more pronounced when the substituent groups are placed on both sides of the triply-bonded linkage as in dimethylacetylene. For this compound these frequencies appear at $\Delta\bar{\nu}$ 2234(10) and 2312(5). Of these, the one at 2123 in methylacetylene and 2312 in dimethylacetylene corresponds to the symmetrical linear vibration of the groups in respect to the triple bond. The $\Delta\bar{\nu}$ 2234 is presumed to be a linear asymmetrical oscillation. If this interpretation is correct, the effect of substitution must be to increase the force constant corresponding to the triply-bonded linkage, as the increase in mass would be in the opposite direction.

Not only is there an effect on the carbon-to-carbon linkage in these compounds, but there is also a noticeable difference in the carbon-to-hydrogen linkage. This increases to $\Delta\bar{\nu}$ 3305 in methylacetylene, which is almost that equivalent to the C—H and N—H frequencies, and likewise indicates a strengthening of the C—H force constant. In methylacetylene a shift occurs at $\Delta\bar{\nu}$ 929 which is probably due to the linear vibration of the methyl

group against the rest of the molecule. In Table 24 are given the frequency shifts for methylacetylene and the modes of vibration which give rise to these frequencies. Glockler and Davis⁶⁰² have analyzed these vibrations in methylacetylene and conclude that there are 11 Raman frequencies of a possible 15, one of which can be interpreted as an overtone. Crawford assigns ten frequencies to the fundamental vibrations of methyl acetylene, of which $\Delta\bar{\nu}$ 926, 1380, 2125, 2910 and 3300 are non-degenerate and 333,

Table 24.—The Raman Shifts in Methyl Acetylene and the Modes of Vibration which Give Rise to Them.

Modes of Vibration	$\Delta\bar{\nu}$	Intensity
(H ₃ C) ↓ —C ↑ :C ↑ —H ↓	336	9(b)
(H ₃ C) ↓ —C ↑ : (CH) ↓	643	5(b)
(H ₃ C) → — ← (C:CH)	929.5	8(s)
H ↑ —H ₂ ↓ —(C—C:C) ↑ —H ↓	1382.5	6(b)
H ↑ —H ↓ —(HC—C:CH)	1448	2(b)
(H ₃ C)—C → : ← C(H)	2123.5	11(s)
(H ₃) → — ← (C—C:C)—H →	2867	6(s)
(H ₃) → — ← (C—C:CH)	2926.2	10(s)
H → — ← (H ₂ C—C:CH)	2971	4(b)
(H ₃ C—C:C) → — ← H	3305	2(s)

642, 1035, 1444 and 2975 are degenerate. Of these the lines which are markedly polarized are $\Delta\bar{\nu}$ 926, 2125 and 2910, corresponding to the valence vibrations of the C—C, C≡C and C—H groups respectively. Bourguel and Daure,^{267, 268} Grédy^{648, 649, 650} and Glockler and Wall⁶¹⁵ have investigated the effect of substitution on the acetylenic linkage, and Blanche Grédy has prepared and examined a large number of acetylenes and has discussed them in considerable detail.

It may be pointed out in general that the "true" acetylenes, that is those containing at least one hydrogen atom attached to a triply-linked carbon atom, exhibit a constant frequency at $\Delta\bar{\nu}$ 2119, which becomes at least two constant frequencies somewhat more elevated in the disubstituted compounds. Some of the reasons for the increase in the number of acetylenic shifts on substitution will be discussed later. At the moment we are more concerned with the delineation of organic structure from an empirical point of view. Disregarding acetylene itself, there is one class of compounds which produces an appreciable effect on the constancy of the acetylenic shift, over and above the effect of the introduction of an organic radical. This includes the compounds which contain ethylenic groups closest to the acetylenic linkage. This is shown in vinylacetylene by a reduction of the average frequency near $\Delta\bar{\nu}$ 2118 to 2098, and in phenylacetylene where the reduction is of a lesser amount, *i. e.*, to $\Delta\bar{\nu}$ 2111, but is still appreciable. In methylphenylacetylene there is a diminution from $\Delta\bar{\nu}$ 2238 to 2214 and at the same time an appearance of $\Delta\bar{\nu}$ 2253 in

place of 2304. If the ethylenic or acetylenic groups are more distantly removed, as in benzylacetylene and 1,8-nonadiene, little influence is exerted. These effects are illustrated in Table 25.

On considering the changes which may take place when a carbinol group is substituted for a hydrocarbon, it is apparent that there is little effect in the "true" acetylenes, and there is but a slight decrease amounting to 10 to 15 wave numbers in the carbinol derivatives of the disubstituted acetylenes where these derivatives are primarily alcohols. If one of the substituents is a phenyl group, then in place of $\Delta\bar{\nu}$ 2214(10) observed for methylphenylacetylene, or 2227(7) in the other disubstituted alcohols, there appears $\Delta\bar{\nu}$ 2198(2) for 3-phenyl-2-propin-1-ol.

However, if the substituent carbinol group represents a secondary alcohol of the general form $R-C\equiv C-CHOHCH_3$, there is an increase of about 20 wave numbers, compared to the primary alcohols, in the two observable acetylenic frequencies. The phenyl derivative of these secondary carbinols likewise shows an anomaly in giving rise to only a single frequency of $\Delta\bar{\nu}$ 2233. Still more remarkable is the observation that, in alcohols represented by $R-C\equiv C(CH_3)_2OH$, in place of two characteristic frequency shifts there occurs only one, $\Delta\bar{\nu}$ 2238(10).

It is again demonstrated in the ether derivatives that if only one hydrogen is attached to the carbon of the acetylenic group, as in the "true" acetylenes, only one acetylenic frequency results. In 3-methoxy-1-propyne this occurs at $\Delta\bar{\nu}$ 2118 which is the same frequency observed in similarly constituted alcohols and hydrocarbons. The simpler derivatives such as 1-methoxy-2-octyne, in which the single hydrogen atom is replaced with a hydrocarbon chain, give rise to three frequencies, namely, $\Delta\bar{\nu}$ 2116(5), 2237(5) and 2282(8). Thus, by increasing the length of the chain on both sides of the acetylenic linkage, there is a doubling of the frequency in the hydrocarbons, and a modification of these doublet frequencies in the alcohols and a tripling in the simple ethers. A change from primary to secondary alcohols augments the two characteristic frequencies. A similar change from primary to secondary ethers causes a more profound effect. The lowest characteristic acetylenic frequency observable, and the highest one, are increased and there is a complete disappearance of the intermediate Raman shift. The tertiary ethers, similar to the tertiary alcohols, yield only one frequency, which occurs at approximately the same value and with the same intensity as the equivalent displacement in the alcohols and one of the frequencies in the hydrocarbons. The presence of a phenyl group directly attached to one of the acetylenic carbons decreases the first or lowest frequency. The second frequency remains relatively unchanged and the third is entirely eliminated. In comparison with the primary alcohols, this behavior is only very roughly similar

Table 25.—The Effect of Substitution on Acetylenic Frequencies.

Hydrocarbons		
I		
$\text{CH}\equiv\text{CH}$	1960(5)	
$\text{CH}_3\text{C}\equiv\text{CH}$	2123(7)	
$\text{CH}_2=\text{CHC}\equiv\text{CH}$	2098(7)	
$\text{C}_4\text{H}_6\text{C}\equiv\text{CH}$	2121(7)	
$(\text{CH}_3)_2\text{CHCH}_2\text{C}\equiv\text{CH}$	2118(7)	
$\text{C}_6\text{H}_{11}\text{C}\equiv\text{CH}$	2118(7)	
$\text{C}_6\text{H}_{13}\text{C}\equiv\text{CH}$	2119(7)	
$\text{HC}\equiv\text{C}(\text{CH}_3)_2\text{C}\equiv\text{CH}$	2118(7)	
$\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$	2116(10)	
$\text{C}_6\text{H}_9\text{CH}_2\text{C}\equiv\text{CH}$	2119(10)	
$\text{C}_6\text{H}_9\text{C}\equiv\text{CH}$	2111(10)	
$\text{C}_6\text{H}_5\text{CH}_2\text{C}\equiv\text{CH}$	2120(8)	
$\text{C}_6\text{H}_{11}\text{C}\equiv\text{CH}$	2118(7)	
$\text{C}_6\text{H}_{11}\text{CH}_2\text{C}\equiv\text{CH}$	2118(7)	
II		
$\text{CH}_3\text{C}\equiv\text{CCH}_3$	2234(10)	
$\text{C}_2\text{H}_5\text{C}\equiv\text{CCH}_3$	2238(10)	
$\text{C}_6\text{H}_5\text{C}\equiv\text{CCH}_3$	2238(10)	
$\text{C}_4\text{H}_9\text{C}\equiv\text{CCH}_3$	2235(10)	
$\text{C}_6\text{H}_{11}\text{C}\equiv\text{CCH}_3$	2233(10)	
$\text{C}_6\text{H}_{13}\text{C}\equiv\text{CCH}_3$	2233(10)	
$\text{C}_6\text{H}_9\text{C}\equiv\text{CCH}_3$	2239(10)	
$\text{C}_6\text{H}_9\text{CH}_2\text{C}\equiv\text{CCH}_3$	2234(10)	
$\text{C}_6\text{H}_5\text{C}\equiv\text{CCH}_3$	2214(10)	
$\text{C}_6\text{H}_{11}\text{C}\equiv\text{CCH}_3$	2239(10)	
$\text{C}_6\text{H}_{11}\text{CH}_2\text{C}\equiv\text{CCH}_3$	2235(7)	
III		
$\text{C}_6\text{H}_{11}\text{C}\equiv\text{CCCH}_3$	2312(5)	2301(5)
$\text{C}_6\text{H}_{11}\text{C}\equiv\text{CC}_2\text{H}_5$	2304(5)	2232(8)
$\text{C}_6\text{H}_{13}\text{C}\equiv\text{CC}_2\text{H}_5$	2304(5)	2234(7)
$\text{C}_6\text{H}_9\text{C}\equiv\text{CC}_2\text{H}_5$	2303(5)	2231(7)
$\text{C}_6\text{H}_5\text{C}\equiv\text{CCCH}_3$	2301(5)	2253(10)
$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_2\text{H}_5$	2303(5)	2210(5)
$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_2\text{H}_7$	2320(1)	2210(2)
$\text{C}_6\text{H}_{13}\text{C}\equiv\text{CCCH}_3$	2302(5)	2233(10)
$\text{C}_6\text{H}_{13}\text{C}\equiv\text{CC}_2\text{H}_5$	2280(1)	2238(7)
$\text{C}_6\text{H}_{13}\text{C}\equiv\text{CC}_2\text{H}_7$	2253(10)	2305(5)
$\text{C}_6\text{H}_{11}\text{C}\equiv\text{CC}_2\text{H}_7$	2259(2)	2232(7)
$\text{C}_6\text{H}_{13}\text{C}\equiv\text{CC}_2\text{H}_9$	2303(5)	2233(7)
$\text{C}_6\text{H}_{13}\text{C}\equiv\text{CC}_2\text{H}_9$		2294(2)
Ethers		
$\text{HC}\equiv\text{CCH}_2\text{OCH}_3$	2118(10)	
$\text{C}_6\text{H}_{11}\text{C}\equiv\text{CCH}_2\text{OCH}_3$	2200(5)	
$\text{C}_6\text{H}_5\text{C}\equiv\text{CCH}_2\text{OCH}_3$	2216(5)	
$\text{C}_6\text{H}_{11}\text{C}\equiv\text{CCH}_2\text{OCH}_3$	2215(5)	
$\text{C}_6\text{H}_9\text{CH}_2\text{C}\equiv\text{CCH}_2\text{OCH}_3$	2216(5)	
$\text{C}_6\text{H}_9\text{CH}_2\text{C}\equiv\text{CCH}_2\text{OCH}_3$	2217(5)	
$\text{C}_6\text{H}_5\text{C}\equiv\text{CCH}_2\text{OCH}_3$	2200(5)	
Alcohols		
$\text{HC}\equiv\text{CCH}_2\text{OH}$	2118(10)	
$\text{HC}\equiv\text{CC}(\text{CH}_3)_2\text{OH}$	2120(8)	
$\text{C}_6\text{H}_{11}\text{C}\equiv\text{CCH}_2\text{OH}$		2226(7)
$\text{C}_6\text{H}_{13}\text{C}\equiv\text{CCH}_2\text{OH}$		2227(7)
$\text{C}_6\text{H}_9\text{CH}_2\text{C}\equiv\text{CCH}_2\text{OH}$		2227(10)
$\text{C}_6\text{H}_{11}\text{CH}_2\text{C}\equiv\text{CCH}_2\text{OH}$		2228(7)
$\text{C}_6\text{H}_5\text{C}\equiv\text{CCH}_2\text{OH}$	2198(2)	2239(10)
$\text{C}_6\text{H}_5\text{C}\equiv\text{CCH}_2\text{OH}$		2290(8)
$\text{C}_6\text{H}_{11}\text{C}\equiv\text{CCH}_2\text{OH}$		2289(8)
$\text{C}_6\text{H}_9\text{CH}_2\text{C}\equiv\text{CCH}_2\text{OH}$		2289(8)
$\text{C}_6\text{H}_{11}\text{CH}_2\text{C}\equiv\text{CCH}_2\text{OH}$		2290(8)

II	$C_6H_{11}C \equiv CCHOHCH_3$ $C_6H_{11}C \equiv CCHOHCH_3$ $C_6H_9CH_2C \equiv CCHOHCH_3$ $C_6H_{11}C \equiv CCHOHCH_3$ $C_6H_{11}CH_2C \equiv CCHOHCH_3$ $C_6H_9C \equiv CCHOHCH_3$	2250(8) 2250(10) 2249(10) 2237(8) 2250(10) 2233(10)	2312(1) 2310(1) 2303(1) incomplete 2314(1)
III	$C_6H_{11}C \equiv CC(CH_3)_2OH$ $C_6H_{11}C \equiv CCOH(CH_3)C_2H_5$ $C_6H_{11}CH_2C \equiv CC(CH_3)_2OH$ $C_6H_9C \equiv CC(CH_3)_2OH$ $(C_6H_{11}C \equiv C)_2CHOH$ $(C_6H_{11}C \equiv C)_3COH$	2239(10) 2238(10) 2237(10) 2230(10) 2250(7) 2236(7)	2304(1)
	Halogen derivatives		
	$Cl \equiv Cl$ $C_6H_5C \equiv CCl$	2109(8) 2225(10)	
	Acids		
	$HC \equiv CCOOH$ $CH_3C \equiv CCOOH$	2122(10) 2243(10)	
III	$C_6H_{11}C \equiv CCH(OCH_3)CH_3$ $C_6H_9CH_2C \equiv CCH(OCH_3)CH_3$ $C_6H_{11}CH_2C \equiv CCH(OCH_3)CH_3$ $C_6H_9C \equiv CCH(OCH_3)CH_3$	2240(10) 2239(7) 2241(10) 2221(10)	2308(1) 2304(1) 2307(1) 2241(10)
IV	$C_6H_{11}C \equiv CC(CH_3)_2OCH_3$ $C_6H_{11}C \equiv CC(CH_3)(C_2H_5)OCH_3$ $C_6H_{11}CH_2C \equiv CC(CH_3)_2OCH_3$ $C_6H_9C \equiv CC(CH_3)_2OCH_3$	2236(10) 2236(10) 2234(10) 2215(7)	2238(10)
V	$HC \equiv CCH-CH_2$  $HC \equiv CH-CHCH_2Cl$ 	2126(7) 2138(7) 2253(5)	

because, with the phenyl-substituted primary alcohols, either there is an equivalent reduction in the lowest frequency and the appearance of a new one at $\Delta\bar{\nu}$ 2239, or $\Delta\bar{\nu}$ 2198 represents a new frequency. It is more likely in the alcohol that $\Delta\bar{\nu}$ 2198 represents a reduction of the frequency normally occurring at $\Delta\bar{\nu}$ 2228. The phenyl derivatives of the secondary ethers possess two frequencies, while the equivalent alcohols possess but one. Likewise in the tertiary phenyl ether compounds $\Delta\bar{\nu}$ 2215(7) and 2238(10) occur in contrast to $\Delta\bar{\nu}$ 2230(10) of the tertiary alcohols.

The effect of adding the ethereal oxygen in the form of a ring structure as in 3,4-epoxy-1-butene is to increase slightly the expected frequency in both the "true" derivative and in the diepoxy compound. With the latter compound exemplified by 1,2,5,6-diepoxyhexene it is interesting to note that only one shift is recorded in contrast to three for the normal ethers.

Relatively few esters have been investigated. These are chiefly methyl α -octynoate and methyl α -nonynoate. These yield a single frequency at $\Delta\bar{\nu}$ 2238(10), although Ballus (Raman Jubilee volume) reports more than one shift for tetrolic and propiolic acids and their methyl and ethyl esters in this region. The halogen derivatives of acetylene are confined to diiodoacetylene and 1-chloro-2-phenylacetylene. As is to be expected, there is a marked diminution in the di-iodo-compound as compared with either acetylene itself or the hydrocarbon derivatives.

From a purely empirical point of view the modifications in the ethylenic frequencies as a function of substitution are of considerable interest in a delineation of the structure of compounds containing this group. It can be readily seen that in the hydrocarbons the mono- and di-substituted compounds may be easily differentiated. These hydrocarbon derivatives likewise may be readily distinguished from the carbinol, ether, ester or halogen derivatives. With the exception of part of the hydrocarbons in a given homologous series, primary, secondary and tertiary compounds may be distinguished from one another. In general the modifications of the acetylenic frequencies follow to some extent the same order as a function of the nature of the substituent groups, as has been observed with the ethylenic frequencies. The acetylenic linkage, however, is much more sensitive to substitution as far as the magnitudes of the shifts are concerned. From a theoretical point of view the multiplicity of the frequencies and their variations are not clearly understood. The assignment of characteristic frequency to a particular binding at least partially ignores the influence of the rest of the molecule. These frequencies arise from the vibrations of the molecules as a whole, and consequently the rest of the molecule gives rise to some modifications. Except in general terms the amount and magnitude of the modifications cannot be anticipated.

The most generally acceptable theoretical explanation of the multi-

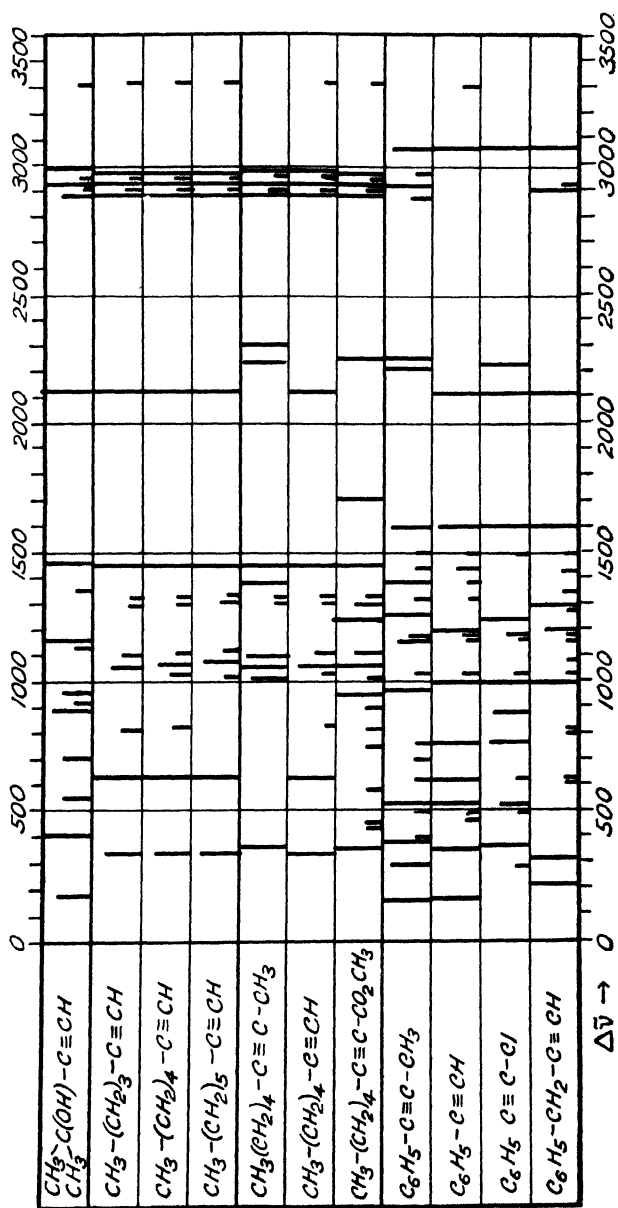


FIGURE 35. Raman Spectra of Some Acetylenic Compounds
(after Bourguet and Daure).

plicity of the acetylenic frequencies in the substituted compounds is one which attributes the splitting of the Raman line to a Fermi resonance⁷⁷ reaction between the acetylenic fundamental and the overtone of another vibration whose frequency must be approximately equal to some sub-multiple of $\Delta\tilde{\nu}$ 2271.

The anomalous effect of the phenyl group on the acetylenic vibration is undoubtedly connected with the presence of the double bonds in this radical. The conjugation of an ethylenic linkage with an acetylenic linkage produces a pronounced effect, as has been shown with vinylacetylene. While attention has been directed, up to this point, almost entirely to the acetylenic linkage in these compounds, the displacement attributed to this linkage is not the only criterion of identification. Bourguel and Daure²⁶⁷ and Grédy⁶⁵⁰ have pointed out that other frequencies also are quite characteristic of the normal acetylenes. The $\Delta\tilde{\nu}$ 340 is generally present in the molecule, and $\Delta\tilde{\nu}$ 375 and 1380 in the disubstituted compounds, and are almost equally characteristic frequencies. In Figure 35 are given the complete Raman spectra for a typical group of these acetylenic compounds.

Chapter 14

The Raman Spectra of Some Cyclic Compounds

Saturated Cyclic Hydrocarbons

The simplest of the cyclic compounds are the cyclopropanes. As far as the carbon atoms are concerned, cyclopropanes can be considered as a system of three masses situated on the corners of a triangle. By assuming equal forces and an equilateral triangle Yates¹⁷⁴⁵ calculated the probable frequencies with mediocre agreement with the observed values. Bhagavantam,¹²⁶ on the assumption that the force constant remained unchanged, has calculated that the ratio of the principal C—C frequencies should be as $\sqrt{2}$. This follows from the fact that the normal frequencies of a system of the type X_3 are given by $\Delta\bar{\nu}_1 \propto \sqrt{\frac{3k}{2M}}$ and $\Delta\bar{\nu}_2 \propto \sqrt{\frac{3k}{M}}$. The observed values for cyclopropane are $\Delta\bar{\nu}$ 1188 and 867 which are in moderate agreement. In Table 26 are given the principal Raman shifts of the cyclo-

Table 26.—The Raman Shifts from Cyclopropanes.

$\begin{array}{c} \text{CH}_2\text{—CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_3\text{—CH—CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2\text{—CH—CH—CH}_2 \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2\text{—CH—CH—C}_2\text{H}_5 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2\text{—CH—CH—C}_6\text{H}_7 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$
736(0)	759(5)	746(5) 765(8) 783(5)	737(5) 746(8) 756(5) 783(1) 813(8) 869(5) 889(5)	760(8) 786(5) 825(1) 861(1)
867(5)	851(5)	866(1)	915(7)	
	892(7)	1035(1) 1173(1) 1214(7)	967(1) 1043(1) 1172(5) 1209(8) 1221(5) 1305(1)	967(5) 1035(8) 1172(1) 1207(7) 1221(5) 1455(7) 2850(5) 2876(7) 2906(7)
1188(10)	1207(7)	1455(7)	2912(7) 2937(7) 2966(7)	2937(7) 2963(7)
1439(1)	1462(1)	2875(7)	2983(5) 2999(10)	3000(10)
2852(0)	2874(5)	2933(7) 2954(7)	2999(10)	3065(7)
	2931(5) 2957(5)	3064(5)	3066(7)	
3011(7) 3029(7) 3076(1)	2998(7) 3074(1)			

propanes omitting some of the very weak lines. Lespieau, Bourguel and Wakeman^{985, 986} have postulated that there is a frequency varying from $\Delta\bar{\nu}$ 1188 to 1214 which remains fairly constant through the series. With the exception of cyclopropane this remains near $\Delta\bar{\nu}$ 1214, and its intensity and uniqueness of position readily facilitate identification of this type of structure. There is another characteristic frequency which varies progressively with the number of carbon atoms in the molecule. This changes from $\Delta\bar{\nu}$ 1188 in cyclopropane to 982 in methylcyclopropane, 915 in dimethylcyclopropane and progressively to $\Delta\bar{\nu}$ 760 in methylpropylcyclopropane, following the equation $\Delta\bar{\nu} = 1188 \times \sqrt{\frac{3}{N}}$ where N is the number of carbon atoms in the molecule. This relationship is probably fortuitous.

From an empirical point of view the C—H linkage in cyclopropane and its derivatives is of considerable interest. This appears between $\Delta\bar{\nu}$ 3064 and 3076 and its intensity increases with increased substitution in the 1,2-position. This cannot be ascribed to the hydrogen of the substituent aliphatic radicals as there is no such frequency occurring in any known derivative or straight-chain aliphatic compound. On the other hand it does seem to be directly connected with the symmetry of the whole molecule for the reason that the intensity of $\Delta\bar{\nu}$ 3074 in methylcyclopropane is not greater than in cyclopropane. Disubstitution increases the intensity. It seems reasonably probable that the origin of this frequency is a ν_s type of oscillation of the hydrogens attached to the CH₂-group. It may be

Table 27.—The Raman Shifts from Some Cyclic Compounds.

Cyclopentane	Methylcyclopentane	$\Delta\bar{\nu}$				
		Cyclohexane	Cycloheptane	Methylcycloheptane	Cyclooctane	Methylcyclooctane
		379	335	320	243	
301						
	523	425	397	381	371	
889	845	801	729	722	700	703
	890					
1032		1029	1005	1000	988	996
1205	1205	1165	1165	1177	1171	1159
1290	1299	1268	1282	1278	1293	1286
1370	1374	1346	1345	1351	1367	1347
1450	1458	1440	1439	1444	1439	1452
2873	2873	2854	2858	2855	2857	2864
2942	2942	2926	2903	2922	2914	2904
2973	2974	2933	2933	2945	2939	2927– 2954

recalled that ethylene oxide gives rise to no such frequency although it is similarly constituted as far as a triangular structure is concerned, but derivatives of ethylene oxide give rise to a frequency slightly less than $\Delta\bar{\nu}$ 3060. There is clearly an analogy between the spatial configuration of these two compounds. Although no saturated aliphatic compounds

have a frequency in this region, it has been shown in the discussion of the olefins that a fairly constant shift appears in the region from $\Delta\bar{\nu}$ 3075 to 3080 in the unsaturated hydrocarbons and at a slightly lower value in the cyclic aromatic compounds. The shift near $\Delta\bar{\nu}$ 3000 also finds a counterpart in the ethylene oxides and the ethylenes, but not in the unsaturated cyclic compounds. Ananthakrishnan^{25, 30} concludes that in cyclopropane the shifts at $\Delta\bar{\nu}$ 3010 and 3028 are polarized, while $\Delta\bar{\nu}$ 3080 as well as $\Delta\bar{\nu}$ 2852 and 1185 are depolarized.

Canals, Godchot and Cauquil³³³ have investigated cyclopropane and other cyclic compounds and Weiler^{1662, 1663, 1664} has investigated cyclopropane. The results of these investigations are given in Table 27.

It is presumed by Canals, Godchot and Cauquil that the characteristic frequency shifts of the five-carbon nucleus of cyclopentane are approximately $\Delta\bar{\nu}$ 1188, 1290, 1268 and 1293. Grédy⁶⁸¹ gives $\Delta\bar{\nu}$ 890, 1020, 1224 and 1305. Piaux¹²³⁷ also considers $\Delta\bar{\nu}$ 890 as characteristic of the cyclopentyl group. Reitz¹³⁶⁶ has dealt extensively with these compounds. For cyclohexane the nuclear shifts are considered to be $\Delta\bar{\nu}$ 440, 801, 1029, 1165 and 1268. With these compounds there exists the possibility of *cis-trans* isomerism. This has been carefully studied by Miller and Piaux,^{1095, 1096} Miller and Lecomte¹⁰⁹⁴ and Lecomte, Piaux and Miller⁹⁷⁶ with some results which are presented in Table 28. These dimethylcyclohexanes show great similarity but there are, nevertheless, notable differences.

While in the region below $\Delta\bar{\nu}$ 1400 in all these compounds there exists a partially characteristic group of frequencies, such as occurs with the carbonyl and ethylenic types of binding, these frequencies are not in the region set apart. Nevertheless, the identifying shifts of these particular types of ring structure have a useful purpose. Certainly they can be used to distinguish one set of homologous series from another. But as far as uniquely identifying an unknown compound is concerned, it is doubtful that they can serve that function. Nevgi and Jatkar¹¹⁶⁵ presume that $\Delta\bar{\nu}$ 1164 and 1355 are characteristic of the *trans* cyclohexyl nucleus, and that $\Delta\bar{\nu}$ 1260 and 1053 are characteristic of the *cis* forms. This view does not seem to be particularly tenable. Hayashi⁷⁰⁹ and Nevgi and Jatkar have also investigated the cyclohexenes as well as the cyclohexanes. In general it is concluded that $\Delta\bar{\nu}$ 600 to 1300 are identifiable with C—C bonds and from 200 to 600 with C—C—C bonds. Donzelot and Barriol⁴⁸⁷ attribute $\Delta\bar{\nu}$ 800, polarized, and $\Delta\bar{\nu}$ 1260, depolarized, to a ring oscillation in cyclohexane.

Oxygen Derivatives of Saturated Cyclic Hydrocarbons

Nevgi and Jatkar¹¹⁶⁵ and Piaux¹²³³ have investigated the oxygen derivatives of cyclohexane such as the cyclohexanols, and Canals, Mousseron,

Table 28.—The Raman Shifts from Some Isomeric Cyclohexanes.

$\Delta\bar{\nu}$					
1,2-Dimethylcyclohexane		1,3-Dimethylcyclohexane		1,4-Dimethylcyclohexane	
<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
	333(2)	253(1)			
			353(1)		
			373(2)	374(5)	372(5)
		407(5)			
415(5)	414(5)	420(8)			
440(5)		446(2)	453(2)	452(5)	463(2)
498(7)			487(1)	473(2)	474(5)
	537(5)	545(8)			
	593(2)				
			625(2)		637(5)
				701(1)	702(1)
749(7)	730(7)	771(7)	752(7)	760(7)	760(7)
				784(1)	787(5)
819(5)			802(1)		
857(5)		847(5)	861(2)		
	842(8)	935(1)	937(2)	927(1)	
950(5)	920(2)	956(1)		951(2)	954(5)
	944(5)	991(2)	980(2)		976(2)
1005(8)	977(8)		1009(2)	1005(1)	1000(5)
	1005(8)	1058(7)	1055(8)	1061(7)	1055(8)
1078(5)	1053(5)		1074(1)		
			1100(2)		1099(5)
	1095(8)	1113(2)			
1164(8)	1159(5)	1165(5)	1163(8)	1163(5)	1163(5)
		1181(5)		1183(5)	
1218(8)	1221(5)	1219(5)	1212(5)		1206(5)
1252(5)	1256(8)			1247(8)	1244(2)
		1269(5)	1266(8)		1263(8)
1292(5)	1302(8)	1303(2)	1305(2)	1307(6)	1301(2)
					1318(1)
1343(8)	1320(8)	1339(5)	1327(1)	1346(8)	1343(8)
1355(8)		1355(2)	1364(1)	1361(2)	
1446(7)	1441(7)	1441(5)	1440(8)	1432(8)	1439(8)
1460(7)	1455(5)	1460(5)	1460(8)	1456(7)	1462(7)
2660(5)					
2844(7)		2845(7)	2846(7)	2848(7)	2853(10)
2854(7)	2854(10)				
	2873(8)	2870(1)	2870(7)	2868(7)	2873(8)
	2894(8)		2883(8)		2898(7)
2915(7)		2912(5)	2912(8)	2907(5)	2913(8)
2931(10)	2927(10)	2929(7)	2928(7)	2926(7)	2930(7)
2950(5)	2959(5)	2955(7)	2960(7)	2952(8)	2960(7)
2975(5)	2973(5)				

Souche and Peyrot^{337, 338} the epoxy-substituted cyclopentanes and cyclohexanes. The simple cyclic compounds such as ethylene oxide have been discussed under the ethers in Chapter 10.

In the cyclopentyl oxygenated compounds Piaux¹²³⁸ has observed $\Delta\bar{\nu}$ 1726(8), 1746(8) for the carbonyl frequency in cyclopentanone; in 2-methylcyclopentanone $\Delta\bar{\nu}$ 1735 and in 3-methylcyclopentanone $\Delta\bar{\nu}$ 1744. These values are slightly higher than those observed in the corresponding

cyclohexane derivatives. There is no evidence of keto-enol tautomerism. The presence of two carbonyl shifts in cyclopentanone is anomalous.

Polarization measurements^{334, 337, 338} on lines whose magnitudes are less than $\Delta\bar{\nu}$ 1460 for the oxygen derivatives indicate that the principal polarized lines occur near $\Delta\bar{\nu}$ 894 and 1388 in the cyclopentane compound and at 840 in the cyclohexyl one, although the total number of polarized lines naturally depends on the kind and position of the substitution.

For the cyclohexane derivatives it is postulated that the shifts $\Delta\bar{\nu}$ 798 to 779 are characteristic of the alcohol grouping. The change in the position of substitution as in *o*-, *m*-, *p*-methylcyclohexanol results in the progressive increase in the frequencies $\Delta\bar{\nu}$ 443, 457, 482, 522, 551 and 649. In the *o*-, *m*-, and *p*-methylcyclohexanones, these are respectively $\Delta\bar{\nu}$ 312, 410, 500, 577, 641 and 692. While the lower frequency differences between $\Delta\bar{\nu}$ 200 and 1000 are significant in differentiating between one compound and another, these particular shifts, unlike others which are characteristic of a particular molecule grouping, cannot be ascribed to a given mode of vibration. The carbonyl shift in the cyclohexanones is approximately $\Delta\bar{\nu}$ 1712 and does not vary with the position of the alkyl radical in the substituted cyclohexanones.¹²³³ In the esters, such as cyclohexyl acetate and cyclohexyl propionate, the carbonyl frequency is $\Delta\bar{\nu}$ 1742 and 1733 respectively. The Raman spectra of various oxygen derivatives have been analyzed in connection with ring strain by Kahovec and Mardaschew.⁷⁹⁶

Cyclopentenes and Hydrocarbon Derivatives

The simplest cycloölefins examined are cyclopentene and cyclopentadiene.^{1364, 1366} Reitz¹³⁶⁴ has investigated by means of mechanical models such molecules as cyclopentane, cyclopentene, cyclopentadiene and their derivatives, and has calculated their vibrational frequencies. These are compared with the experimental ones and with the frequency changes as a function of symmetry properties. These results are both interesting and instructive. According to these authors there is no evidence of an abnormal behavior of the C=C bond in unstrained five-membered rings. In general it is concluded by Reitz that the symmetry of the five-membered rings corresponds to C_{2v} , which is applicable not only to the cycloölefins but to pyrrole, furan and thiophene. These conclusions are subject to slightly different interpretations depending on the compound involved. A number of weak lines, all of which are depolarized, are observed in cyclopentadiene, namely, $\Delta\bar{\nu}$ 346, 467, 674 and 804. In addition Reitz has recorded $\Delta\bar{\nu}$ 911(4), 956(0), 990(1), 1085(3), 1105(8), 1368(5), 1393(1), 1496(10), 2973(1) and 3088(7). Of these $\Delta\bar{\nu}$ 1105 has a depolarization constant of 0.31. The shifts at $\Delta\bar{\nu}$ 1368, 1496 and 3088 are also considered polarized. These

results are in modest agreement with those of Truchet and Chapron.¹⁵⁷⁸

For the polymeric cyclopentadienes were observed $\Delta\bar{\nu}$ 675(3), 774(3), 936(3), 954(3), 1124(3), 1137(3), 1439(3), 1574(4), 1614(4), 2069(2) and 3058(2). The particular feature in connection with cyclopentadiene is the shift $\Delta\bar{\nu}$ 1500 attributable to the ethylenic linkage. While this large decrease is not analogous to that observed with the allenes, it is much lower than that observed in other unsaturated cyclic hydrocarbons.

Godchot, Canals and Cauquil^{618, 619, 620} have investigated a series of cycloolefins, and Piaux,^{1234, 1235, 1236, 1237} Weiler¹⁶⁶⁴ and Reitz¹³⁶⁶ have investigated cyclopentene and its derivatives in particular. In Table 29 are

Table 29.—The Raman Shifts from Cyclopentene and its Derivatives.

$\Delta\bar{\nu}$				
Cyclopentene	1-Methylcyclopentene	1-Ethylcyclopentene	1-Phenylcyclopentene	Benzylcyclopentene
				210(8) 231(5)
	325(5)	336(5)	339(5)	
385(3)		404		
608(0)	578(8)		619(5)	622(5)
696(1)	851(5)			
772(0)	881(8)	867		
900(8)	903(5)	906	958(5)	968(5)
964(8)	966(0)	949	982(5)	
	1008(8)	993	1004(7)	1003(10)
1025(5)	1026(5)	1031(7)	1033(5)	1030(8)
1108(7)		1131		
			1157(5)	1155(5)
			1184(5)	1181(5)
1207(5)	1207(8)	1200(5)	1208(7)	1205(5)
	1259(5)			
1296(5)	1295(5)		1296(8)	
	1333(8)		1342(5)	
	1383(8)	1385		
1441(7)	1439(10)		1442(8)	1441(7)
		1445(8)		
1467(5)	1465(8)		1495(8)	1466(5)
1615(7)		1660(10)	1600(10)	1603(10)
	1658(10)		1627(10)	1652(10)
2857(7)	2848(10)	2844(8)	2845(7)	2846(7)
2878(5)		2858(5)		
2913(7)	2910(10)		2897(8)	2902(7)
			2926(8)	
2953(7)	2959(8)	2966(7)	2955(8)	2960(7)
				3037(8)
3060(7)	3045(8)	Incomplete	3061(10)	3060(8)

given the principal Raman lines of cyclopentene and four of its hydrocarbon derivatives based on the data of Piaux and of Godchot, Canals and Cauquil. It is noticeable that the ethylenic shift in cyclopentene, namely $\Delta\bar{\nu}$ 1615, is approximately 27 wave numbers lower than the average ethylenic shift in the aliphatic hydrocarbons of the type $R-CH=CH_2$ as given in Table 12. With substitution on the carbon atom adjacent to the double bond in

cyclopentene the frequency is increased to $\Delta\bar{\nu}$ 1658, a value more comparable with the ethylenic shift obtained in compounds of the type $R-CH=CH-R'$. If the substituent is a phenyl radical, the augmentation in the double bond shift as compared with cyclopentene is less marked, becoming $\Delta\bar{\nu}$ 1627; but if the phenyl radical is one carbon atom removed from the ethylenic group, as in benzyl- Δ^1 -cyclopentene, the shift is $\Delta\bar{\nu}$ 1652. In other words, the effect of the phenyl radical does not persist through an intermediate carbon atom.

The characteristic hydrogen-to-carbon shift in unsaturated aliphatic compounds, it will be remembered, was $\Delta\bar{\nu}$ 3005 and 3080, as given in Tables 12 and 13. This type of hydrogen frequency appears strongly in all the cyclopentenenes at about $\Delta\bar{\nu}$ 3055.

In 1-methyl- Δ^2 -cyclopentene the ethylenic shift occurs at $\Delta\bar{\nu}$ 1613 instead of near 1660, but in all cases it is strongly polarized.³³⁸ The other partially polarized lines are those near 966 and 900. The high degree of polarization of the ethylenic shift is significant in that it indicates a normal symmetrical vibration of the $C=C$ linkage.

Oxygen Derivatives of Cyclopentenenes

The oxygenated derivatives of these cyclopentenenes yield the results indicated in Table 30. For the alcohols there is no indication of an $O \leftrightarrow H$ shift. This is probably due to its weakness. In Δ^1 -cyclopentylaldehyde and in methyl Δ^1 -cyclopentylcarboxylate, the carbonyl group is conjugated with the ethylenic group. This has a decided effect on both of these frequencies. The ethylenic frequency which is at approximately $\Delta\bar{\nu}$ 1660 in the methyl derivative of cyclopentene reverts to $\Delta\bar{\nu}$ 1616 in the aldehyde and 1631 in the acid. At the same time the normal aliphatic aldehyde shift at $\Delta\bar{\nu}$ 1720 appears at 1676 and the carbonyl shift in the normal ester, which occurs near $\Delta\bar{\nu}$ 1735, is shifted to 1715. This diminution in the carbonyl shift is similar to the effect observed in the unsaturated straight-chain carbonyl compounds when there is a conjugation of these two frequencies. In general the modifications in the ethylenic shift observed in the cyclopentenenes show approximately the same relative order as those observed by Bourguel for the modifications of this shift in the aliphatic ethylenes. In the cyclic compounds, however, these modifications are more pronounced. This is particularly noticeable toward the extremes of the two respective series. Radicals generally considered negative, such as acid, ester and aldehyde groups, tend to decrease the value of the ethylenic frequency, while on the other hand, radicals considered positive, such as alkyl groups, increase the frequency.

The effect of this substitution on the characteristic frequency shifts for the cyclopentene nucleus is given in Table 31 from the data of Piaux,¹²³⁷

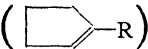
Table 30.—The Raman Shifts from Oxygen Derivatives of Some Cyclopentenenes and Cyclohexenes.

Compounds	Raman Shifts									
	221 (3)	329 (8)	366	420 (5)	482 (2)	470 (3)	506 (5)			
Δ^1 Cyclopentylcarbinol			366	420 (5)	482 (2)					
Δ^1 Cyclopentylethanol			385 (3)		470 (3)		506 (5)			
Δ^1 Cyclopentylpropanol			365 (2)							
Δ^1 Cyclopentenealdehyde			381 (5)		480 (7)					
Methyl- Δ^1 -cyclopentenecarboxylate	165 (3)		378 (5)							
Δ^1 -Cyclopentylcarbinolacetate										
1-Methyl- Δ^1 -cyclohexen-6-ol			320 (2)	418 (3)						
1-Ethyl- Δ^1 -cyclohexen-6-ol			343 (5)	432 (5)	474 (5)	542 (3)	584 (5)	609 (3)		
1-Methyl- Δ^1 -cyclohexen-6-one			304 (1)	358 (1)	478 (3)	554 (3)	611 (1)			
Ethyl- Δ^1 -cyclohexen-6-one	205 (3)		296 (3)	411 (2)	472 (5)	526 (7)	600 (2)			
1-Methyl-6-ethoxy- Δ^1 -cyclohexene			302 (3)		485 (3)	595 (1)				
Ethyl- Δ^1 -cyclohexen-6-yl acetate				425 (1)	473 (1)					
				401 (1)	545 (1)		618 (3)			
Δ^1 Cyclopentylcarbinol			792 (1)	826 (1)						
Δ^1 Cyclopentylethanol					870 (5)	888 (7)	933 (2)	949 (2)	983 (5)	
Δ^1 Cyclopentylpropanol					853 (8)	893 (8)	948 (7)	985 (2)		
Δ^1 Cyclopentenealdehyde					854 (5)	895 (7)	950 (7)			
Methyl- Δ^1 -cyclopentenecarboxylate			769 (3)			882 (5)	954 (7)	967 (5)		
Δ^1 -Cyclopentylcarbinolacetate	636 (3)									
1-Methyl- Δ^1 -cyclohexen-6-ol	637 (5)		688 (3)		870 (5)	889 (5)	907 (5)	956 (2)		
1-Ethyl- Δ^1 -cyclohexen-6-ol	645 (1)		747 (5)	826 (2)	838 (2)	889 (5)	907 (5)	956 (2)		
1-Methyl- Δ^1 -cyclohexen-6-one	629 (3)	645 (1)	707 (5)	807 (2)	855 (5)	895 (3)	910 (3)	948 (2)	982 (2)	
Ethyl- Δ^1 -cyclohexen-6-one	635 (3)	655 (3)	710 (5)	849 (5)	875 (5)	886 (3)	918 (5)	963 (3)		
1-Methyl-6-ethoxy- Δ^1 -cyclohexene			672 (3)	862 (2)	879 (5)	885 (2)	907 (5)	972 (3)		
Ethyl- Δ^1 -cyclohexen-6-yl acetate				820 (3)	852 (3)	911 (3)				
				792 (3)	841 (2)	877 (2)				
				787 (1)	851 (8)		921 (8)	998 (3)		
Δ^1 Cyclopentylcarbinol	1022 (5)		1080 (1)	1133 (3)						
Δ^1 Cyclopentylethanol	1006 (5)		1079 (5)		1160 (5)	1207 (7)	1231 (2)			
Δ^1 Cyclopentylpropanol	1029 (5)				1159 (2)	1206 (9)	1226 (3)			
Δ^1 Cyclopentenealdehyde										
Methyl- Δ^1 -cyclopentenecarboxylate	1023 (2)				1125 (3)	1205 (2)	1232 (2)			
Δ^1 -Cyclopentylcarbinolacetate	1025 (7)				1158 (5)	1206 (5)	1245 (2)			
						1206 (5)				

1-Methyl- Δ^1 -cyclohexen-6-ol	1005(5)	1015(5)	1035(5)	1062(5)	1089(2)	1102(5)	1154(3)	1168(2)	1186(5)	1216(2)
1-Ethyl- Δ^1 -cyclohexen-6-ol				1051(8)	1080(5)				1183(5)	1217(3)
1-Methyl- Δ^1 -cyclohexen-6-one		1023(5)		1055(2)	1083(5)	1110(3)	1142(2)		1175(5)	1243(3)
Ethyl- Δ^1 -cyclohexen-6-one				1057(5)	1093(5)				1175(5)	1248(5)
1-Methyl-6-ethoxy- Δ^1 -cyclohexene		1013(3)	1032(3)	1060(3)	1089(3)	1126(3)	1160(3)		1185(2)	1217(2)
Ethyl- Δ^1 -cyclohexen-6-yl acetate		1021(1)		1065(5)					1188(5)	
Δ^1 Cyclopentylcarbinol			1296(5)					1385(3)		1443(8) 1466(5)
Δ^1 Cyclopentylethanol	1250(2)		1294(5)		1318(2)	1343(1)		1385(3)		1444(10) 1468(7)
Δ^1 Cyclopentylpropanol			1294(5)			1343(3)		1383(3)		1441(8) 1464(7)
Δ^1 Cyclopentenaledehyde			1289(5)				1351(2)	1383(7)		1434(7)
Methyl- Δ^1 -cyclopentenecarboxylate		1272(2)	1297(5)			1334(3)	1356(2)			1437(8) 1469(5)
Δ^1 -Cyclopentylcarbinolacetate			1296(5)		1320(8)		1360(2)	1382(2)		1443(8) 1466(5)
1-Methyl- Δ^1 -cyclohexen-6-ol	1255(5)			1300(5)	1312(5)	1337(3)	1356(2)	1379(5)		1436(8) 1457(7)
1-Ethyl- Δ^1 -cyclohexen-6-ol	1253(3)	1271(8)		1300(5)		1347(5)		1381(3)		1433(10) 1451(8)
1-Methyl- Δ^1 -cyclohexen-6-one	1255(2)				1322(2)		1360(7)			1434(8) 1456(5)
Ethyl- Δ^1 -cyclohexen-6-one				1308(1)		1345(3)		1380(5)		1434(8) 1460(5)
1-Methyl-6-ethoxy- Δ^1 -cyclohexene	1254(5)	1273(3)		1306(5)		1335(3)	1354(3)	1372(7)	1402(3)	1437(8) 1450(7)
Ethyl- Δ^1 -cyclohexen-6-yl acetate	1254(5)			1302(5)		1332(5)		1381(5)		1434(10) 1448(10)
Δ^1 Cyclopentylcarbinol			1656(8)		2848(10)		2902(10)		2952(10)	3048(5)
Δ^1 Cyclopentylethanol			1651(10)		2848(10)		2901(10)		2932(10) 2956(7)	3051(7)
Δ^1 Cyclopentylpropanol			1650(8)		2848(8)	2876(5)	2908(8)		2937(8)	3052(5)
Δ^1 Cyclopentenaledehyde		1616(10)	1676(10)			incomplete				
Methyl- Δ^1 -cyclopentenecarboxylate		1631(8)		1715(8)	2844(8)	2894(7)	2915(7)		2954(10)	3072(7)
Δ^1 -Cyclopentylcarbinolacetate				1743(5)	2851(10)			2940(10)		3058(7)
1-Methyl- Δ^1 -cyclohexen-6-ol			1658(8)			2872(8)	2914(8)	2943(8)		
1-Ethyl- Δ^1 -cyclohexen-6-ol			1670(8)		2837(8)					
1-Methyl- Δ^1 -cyclohexen-6-one		1640(8)	1667(10)			incomplete			2950(7)	
Ethyl- Δ^1 -cyclohexen-6-one		1636(10)	1670(8)			2878(7)	2924(7)			
1-Methyl-6-ethoxy- Δ^1 -cyclohexene	1478(3)		1670(10)			incomplete				
Ethyl- Δ^1 -cyclohexen-6-yl acetate			1673(8)		2837(7)	2872(8)	2912(8)	2936(8)		
			1672(10)	1737(5)		incomplete				

and in Table 30 are shown the complete spectra for some oxygen derivatives of both cyclopentene and cyclohexene.

Table 31.—Characteristic Frequencies from Substituted Δ^1 -Cyclopentene

R								
	$\Delta\bar{\nu}$							
H	899(4)	1025(3)	1207(2)	1296(1)	1441(7)	1467(2)	1615(6)	3060(3)
CH ₃	881-903(4)	1026(3)	1207(5)	1295(1)	1439(8)	1465(5)	1658(6)	3045(2)
C ₆ H ₅	890-908(2)	(1033)(10)	1208(6)	1296(4)	1442(6)	1462(1)	1627(8)	(3061)(4)
CH ₂ C ₆ H ₅	887-902(1)	(1030)(10)	1205(2)	1297(3)	1441(7)	1466(2)	1652(8)	3037(3)
CH ₂ OH	888(8)	1022(2)	1202(6)	1296(3)	1443(8)	1466(3)	1656(8)	3048(4)
CH ₂ OCOCH ₃	889-907(4)	1025(3)	1206(3)	1296(1)	1443(8)	1466(6)	1658(8)	3058(3)
CHOHCH ₃	893(10)	1026(1)	1207(4)	1294(2)	1444(8)	1468(5)	1651(8)	3051(3)
CHOHC ₂ H ₅	895(7)	1029(2)	1206(2)	1294(2)	1441(8)	1464(5)	1650(7)	3052(2)
CH ₂ Br			1205(2)		1440(7)		1640(7)	
CHO	882(3)		1205(1)	1289(2)	1434(7)		1616(9)	Broad
COOCH ₃	903(3)	1023(2)	1206(2)	1297(3)	1437(9)	1469(4)	1631(8)	3072(7)
CN	896(7)	1020(2)	1210(3)	1299(3)	1437(9)	1468(4)	1615(8)	3076(8)

Cyclohexenes and Other Cycloölefins

Like most first members of a homologous series, cyclohexene has received considerable attention. It and its derivatives have been examined by Andant,^{41, 42, 43} Godchot, Canals and Cauquil,^{619, 620} Hayashi,⁸⁴³ Lespieau and Bourguel,^{982, 988} Morris,¹¹⁴⁰ Nevgi and Jatkar,¹¹⁶⁵ Weiler,^{1662, 1663, 1664} Wood and Collins,¹⁷²⁴ and Canals, Mousseron, Souche and Peyrot.^{335, 336, 337, 838} Unlike the ethylenic shift in cyclopentene, this shift in cyclohexene is in its average position and is found at $\Delta\bar{\nu}$ 1650. The C—H shift of the cyclic hydrocarbons, which appears near $\Delta\bar{\nu}$ 3060 in cyclopentene and benzene, is reduced to $\Delta\bar{\nu}$ 3024(6) in cyclohexene. This shift was not recorded by Godchot, Canals and Cauquil for this compound or with the other members of the homologous series, although it is possible that it is present. If it is actually entirely absent in the derivatives of cyclohexene there is no obvious explanation. Canals, Mousseron, Souche and Peyrot³³⁵ imply the presence of normal hydrogen frequencies in Δ^1 -substituted cyclohexenes, but no figures are given by them. They observe a line at $\Delta\bar{\nu}$ 997 in cyclohexene which remains approximately constant as also do a pair of lines at $\Delta\bar{\nu}$ 1172-1191 and 1267-1281 in other derivatives, and are apparently characteristic of alicyclic hydrocarbons. The shifts observed for a series of cyclohexenes are indicated in Table 32. No notation is given as to the relative intensities, although $\Delta\bar{\nu}$ 396, 825, 997, 1069, 1220, 1431 and 1655 represent the strong lines in cyclohexene. It is noted that the position of the double bond in the ring influences the ethylenic shift, as indicated in 1-methyl- Δ^3 -cyclohexene. This is compatible with the already established principles indicating that the greater the distance the double bond is from a substituent group, the less effect this group has.

While the other cyclohexenes have a frequency displacement between $\Delta\bar{\nu}$ 1650 and 1680, cyclooctene shows an unusual anomaly in having this frequency at $\Delta\bar{\nu}$ 1604, which is not far removed from that of cyclopentene. This may indicate a weakening of the bond in rings of five or eight carbon atoms as compared with the six- or seven-membered rings. The only strongly polarized line in cyclohexene and its derivatives is $\Delta\bar{\nu}$ 1655–1670.³³⁸ Other partially polarized lines occur near $\Delta\bar{\nu}$ 1340, 1030–1060, 1000 and 800.

Table 32.—The Raman Shifts from Some Cycloolefins.

$\Delta\bar{\nu}$							
Cyclohexene	1-Methyl-cyclohexene	1-Methyl- Δ^1 -cyclohexene	1-Ethyl-cyclohexene	1,4-Di-methyl- Δ^1 -cyclohexene	Cycloheptene	1-Methyl-cycloheptene	Cyclooctene
176	132	145			144		158
273					212		243
					315	305	294
396	437	392		398		386	
451	495	447	439	417			
494	588	495		447			424
	618		625	525		603	
	695			658			
703	758	732	752	757	738	722	695
825	821	791	835	786		796	
		894	852	801			
	859	957	894	894			
997	990	995	993	996	996	996	996
1069	1069		1055		1043	1082	1096
	1087			1095		1120	
1139	1152	1229		1171		1196	1171
1220							
1272	1266	1258	1213	1256	1273	1258	1271
	1309		1381	1295		1323	
1342	1367				1348	1379	
1431	1445	{ 1443 1450	1432	{ 1443 1449	1445	1445	1439
1650	1675	1650	1675	1680	1651	1672	1604
2821							
2868	2876	2803	2817	2807	2867	2861	2864
2914	2914	2914					
2940	2940	2944	2926	2872	2912		2912
	2964	2967	2942	2944	2944	2940	2950
						2966	
3024							

Two cyclohexadienes have been investigated. These are 1,3-cyclohexadiene, examined by Andant,⁴³ Bonino and Manzoni-Ansidei,^{222, 235} Kohlrausch and Seka,⁸⁷¹ and Murray,¹¹⁵⁰ and 1,4-cyclohexadiene, which has been studied by Andant⁴³ and Kohlrausch and Seka.⁸⁷¹ The spectrum for the 1,3-compound, according to Murray, is $\Delta\bar{\nu}$ 298(4), 394(2), 458(1), 505(0), 559(1), 618(1), 823(10), 848(8), 945(4b), 992(15), 1060(2), 1174(4), 1220(3), 1240(2), 1266(1), 1324(1), 1411(1), 1432(5), 1576(20), 1615(3), 2823(8b), 2864(8b), 2908(4), 2936(8), 3018(5), 3041(10) and 3056(7). There are obviously two bonds distinctly ethylenic in character,

corresponding to $\Delta\bar{\nu}$ 1576 and 1615. The first of these is exceedingly low for this type of frequency displacement but it is not so low as the ethylenic observed for cyclopentadiene, namely $\Delta\bar{\nu}$ 1500. The larger displacement is more comparable to that observed in benzene than to that yielded by cyclohexene. Most of the strong lines in benzene have a counterpart in 1,3-cyclohexadiene. In 1,4-cyclohexadiene the strongest shift is practically identical with that of the 1,3-compound. The other ethylenic shift is $\Delta\bar{\nu}$ 1635, and like $\Delta\bar{\nu}$ 1615 is relatively very weak.

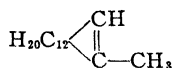
Structurally the essential difference between the 1,3- and 1,4- compounds is a greater degree of symmetry in the 1,4- and the conjugation of the double bonds in the 1,3- compounds. In the straight-chain hydrocarbons the effect of such conjugation is to reduce the value of the ethylenic shift. In these cyclic isomers, however, the strongest shift remains the same but the weaker one is reduced slightly. While there may be some resonance between possible structures for these compounds, there does not seem to be any evidence in favor of any allenic type of linkage. Furthermore, while there is apparently a reduction in the value of the force constant as compared with that observed in unsaturated ethylenic compounds, it is doubtful that this reduction could be characterized by calling the net bond force a bond and a half.

The oxygenated derivatives of cyclohexene show somewhat the same behavior as the similarly substituted cyclopentenes, as is shown in Table 30. There is first an augmentation in the ethylenic frequency from $\Delta\bar{\nu}$ 1650 to 1680, if the substituent is a hydrocarbon radical. Furthermore, if the substituent group is an alcohol, ether or ester, this value near $\Delta\bar{\nu}$ 1670 remains unchanged. The ester behavior is not similar to the cyclopentenyl ester which, as has been pointed out, suffers a reduction in the ethylenic frequency of 45 wave numbers. The ketonic derivatives of the cyclohexenes exhibit a shift close to $\Delta\bar{\nu}$ 1638 for the ethylenic grouping. This decrease of 30 wave numbers is approximately the same amount of reduction as is observed with cyclopentenealdehyde. The carbonyl shift in the ketonic derivatives is also diminished from its normal position in aliphatic compounds from $\Delta\bar{\nu}$ 1705 to 1670. The ester shows no diminution in its carbonyl shift.

It has been pointed out previously that these alterations in the carbonyl and ethylenic frequencies are attributable to the interactions between them in a conjugate system. Here likewise lies the explanation for the different behavior of 1-ethyl- Δ^1 -cyclohexen-6-yl acetate and Δ^1 -cyclopentylcarbinol acetate in comparison with methyl Δ^1 -cyclopentene carboxylate. In the first two of these compounds the ethylenic group is two carbon atoms removed from the ethylenic binding. While cyclopentene and its derivatives exhibit a frequency near $\Delta\bar{\nu}$ 3060 corresponding to the $=C-H$ group-

ing, this frequency is missing in the substituted cyclohexenes but is present in the cyclohexadienes.

One of the most peculiar cycloölefins investigated is cedrene, which presumably has the formula



This compound was investigated by Matsuno and Han.¹⁰⁴⁴ These authors found 119 Raman lines, of which $\Delta\tilde{\nu}$ 1666 is attributed to the ethylenic linkage. A very careful analysis was made of the Raman lines observed and an attempt was made to correlate them with a possible structure. It is supposed that a frequency at $\Delta\tilde{\nu}$ 1375 is associated with the structure $\begin{array}{c} -\text{C}=\text{C}- \\ \parallel \\ \text{CH}_3 \end{array}$. While the results are not conclusive, this is a good example of the method employed in the application of Raman spectra to the delineation of molecular constitution. Other examples will be given after the discussion of benzene and its derivatives.

Chapter 15

The Raman Spectra of Aromatic Hydrocarbons

Benzene

Benzene has been investigated more extensively than any other compound. It is impossible to cite in this text all the contributions of the large number of workers who have examined this compound and its derivatives. The material presented has been chosen with a view to presenting typical effects of substitution and the Raman spectra of some of these compounds rather than a detailed summary of each compound.

Grassmann and Weiler⁶⁴² obtained 41 lines from benzene and believe that these may be explained as a result of ten fundamental frequencies and their combinations. The most characteristic shifts are $\Delta\bar{\nu}$ 992, 1585, 1606, 3049, and 3063. The first of these, $\Delta\bar{\nu}$ 992, was attributed to the carbon-to-carbon vibration; the second two to the ethylenic linkage, and the remainder to the carbon-hydrogen oscillation. With the advent of deuterium substitution in benzene and of polarization measurements on this compound, much progress has been made in the interpretation of its structure. This progress has been ably summarized by Angus, Ingold, Leckie and other co-authors,^{60, 61, 62, 63} who have determined the Raman spectra of benzene and its deuterium derivatives and also have analyzed their absorption and emission spectra. While others have participated in the delineation of the structure of benzene and benzene-d₆ by various methods, emphasis will be placed particularly on this summary referred to above because it represents the most complete presentation, it does not differ widely from the results of other workers where there is duplication, and because of the evident care with which it is done. The results obtained by these authors are summarized in Table 33. As far as benzene is concerned these are in good agreement with the observations of Grassmann and Weiler. The principal omissions have been some of the lines reported by Wood for benzene-d₆ which are probably spurious.

As a first approach to a consideration of the structure of benzene it may be mentioned that at least six structures have been proposed for this substance. These are the structures of Kekulé, Dewar, Claus, Ladenburg, Thielé and Baeyer. It is one of the anomalies in the elucidation of the structure of organic compounds in general that what would seem to be one

Table 33.—Raman Shifts Observed in Benzene and Benzene-d₆.

Benzene				Benzene-d ₆			
	$\Delta\bar{\nu}$	i	ρ		$\Delta\bar{\nu}$	i	ρ
1.	404			1.	337		
2.	606			2.	577	1.2	0.76
3.	685	2.1	0.81	3.	661	1.4	0.87
4.	781			4.	710		
5.	802			5.	750		
6.	824			6.	790		
7.	849	0.9	0.77	7.	867	2.3	0.81
8.	979			8.	945	10	0.08
9.	984			9.	976		
10.	992	10.0	0.9				
11.	999						
12.	1005			10.	1000		
13.	1030						
14.	1178	2.2	0.7				
15.	1285						
16.	1326			11.	1327		
17.	1404			12.	1457		
18.	1449			13.	1530		
19.	1478			14.	1558	2	0.82
20.	1585	1.9	0.81	15.	1586		
21.	1606						
22.	1693			16.	1884		
23.	1988			17.	1931		
24.	2030			18.	2128		
25.	2128			19.	2145		
26.	2293			20.	2264	6	0.7
27.	2358			21.	2292	10	0.35
28.	2454			22.	2461		
29.	2543			23.	2510		
30.	2618			24.	2571		
31.	2688			25.	2739		
32.	2925						
33.	2948						
34.	3047	4.8	D				
35.	3062	10.6	0.4				
36.	3164			26.	3110		
37.	3187		P				
38.	3467						
39.	3680						
40.	3916						

of the simplest applications of Raman spectra, namely, the differentiation of these structures, has not, at least heretofore, met with conspicuous success. Neither has the application of the mechanical models of Andrews and his co-workers entirely solved this problem. As has been indicated previously, it is possible that the rigid chemical methods of depicting formulas are in this case not sufficiently dynamic. On the other hand, it is, of course, easy to assume theoretically dynamic configurations which may or may not be directly connected with reality. Heretofore Raman spectra have preceded rather than followed the interpretation of bonds on the basis of resonance as employed most generally by Pauling. The triple-bond structure of nitrous oxide and possibly of carbon monoxide are pertinent examples.

The interpretations of Angus, Bailey, Ingold and Wilson and the other co-authors in this series of papers will be discussed later. In the meantime a brief resumé of the opinions of other workers, particularly in regard to the ethylenic shift in benzene, will be presented briefly. In the case of benzene it was originally presumed that shifts in the region of $\Delta\tilde{\nu}$ 1585 and 1608 were due to the same type of double bond as found in the ethylenic linkage. Subsequently this was questioned. Wilson^{1690, 1691} in his very competent analysis of the spectrum from a mathematical view, attributes $\Delta\tilde{\nu}$ 1584 to an accidental degeneration. Originally Kettering, Shutts, and Andrews⁸⁰⁸ assumed that the evidence from the vibration of the mechanical models was in favor of the double-bond structure. Murray, Deitz, and Andrews¹¹⁵⁴ conclude that there are no effective forces acting between the carbon atoms *para* to one another in the ring and that this, therefore, is evidence against the centric formula. They further concluded that, with the assumption that the average force constant of the carbon-to-carbon bond in the ring is roughly one and one-half times those of the normal homopolar single bonds, the results are in accord with the resonance formula of Pauling or with the Kekulé formula. Bonino^{203, 205} has discussed the entire situation in regard to benzene in considerable detail. He believes that the line at $\Delta\tilde{\nu}$ 1580 is somewhat analogous to the line $\text{C}=\text{C}$, and it is because of other conditions that there is doubt whether this represents a true double bond. Bonino and Manzoni-Ansidei²³⁵ doubt the existence of ethylenic linkages in benzene. Truchet and Chapron¹⁵⁷⁸ express the view that the shift at $\Delta\tilde{\nu}$ 1584 or 1608 is well within the variation in the $\text{C}=\text{C}$ shift observed in other compounds whose structure is generally accepted as containing a $\text{C}=\text{C}$ group. Lespieau and Bourguel⁹⁸³ and Bourguel²⁶² consider these shifts as arising from doubly-bonded carbon atoms. This shift may actually vary from $\Delta\tilde{\nu}$ 1409 in thiophene to $\Delta\tilde{\nu}$ 1679 in trimethylethylene, excluding $\Delta\tilde{\nu}$ 1074 observed in allene. In any case it does not seem to be tenable that this shift can owe its origin to any carbon and hydrogen vibration, since it is present in pentachlorobenzene and slightly shifted in hexachlorobenzene.

It is believed by many that while the Kekulé notation may represent too static a picture, for the purposes of representing the modifications of Raman spectra as a function of constitution, a shift near $\Delta\tilde{\nu}$ 1600 may be treated in the same fashion as any other $\text{C}=\text{C}$ line. It is difficult to conceive that the method of treating linkages in cyclopentene, cyclohexene, or their respective dienes and the terpenes should be radically different from that for benzene and its derivatives. From the point of view of the analysis of their spectra, therefore, the benzene compounds will be considered in the same fashion as any other hydrocarbons.

Coincidences with Infrared Absorption

So far as the chemical transformations of benzene are concerned the Kekulé configuration is the best single representation. This structure, however, does not satisfactorily interpret the stability of the ring. Neither do the saturated alternatives. Pauling and Wheland have assumed that the atomic nuclei occupy the corners of a plane, regular hexagon, in which case two Kekulé and three Dewar formulas, derived from each other by rotations through 60° , represent the complete set of unperturbed structures. New wave functions may be composed from the wave functions of these structures. The principal objection to this has been that no molecule possessing a centre of symmetry can possess a fundamental, overtone or combination which can appear both in the Raman effect and in infrared absorption spectra. In contradistinction to this it has been shown that there are a number of coincidences between the infrared absorption and the Raman effect, and the authors referred to believe that this number exceeds any possible accidental coincidences. Some of these coincidences depend upon whether benzene is examined in the liquid or the vapor phase. For example, $\Delta\bar{\nu}$ 610, 849, 985, 1170, 1584 and 1604, which are theoretically forbidden in the infrared, form coincidences with the Raman shifts in the immediate neighborhood. There are other coincidences representing infrared fundamentals which appear weakly in the Raman spectra of the liquid substance. These are $\Delta\bar{\nu}$ 1029 and 1477. There are other coincidences in the liquid representing frequencies which by the selection rules are inactive in both spectra, such as $\Delta\bar{\nu}$ 773, 1298 and 2356, which appear only in the infrared. A coincidence has been suggested by Krishnamurti at $\Delta\bar{\nu}$ 3046. The fact is that the liquid band is broad enough to include this, although there is a possibility of a coincidence. There is another possibility that the Raman frequency at $\Delta\bar{\nu}$ 3063 may be coincident with the infrared absorption observed at 3080, although this may happen without prejudice as to the question of whether an infrared absorption band represents a single frequency.

Other coincidences also are observed between the infrared absorption and the Raman spectrum of benzene- d_6 of which at least five represent Raman fundamentals which appear in the liquid infrared spectrum but not in the gaseous spectrum. On the whole there are only two principal coincidences, $\Delta\bar{\nu}$ 3063 and 2294, which are not demonstrably accidental or due to the use of liquids. The conclusion from this discussion is that there are *no coincidences which need convey any suggestion of the absence of symmetry from these molecules.*

Therefore, the objection, made originally by Placzek,¹²⁴³ to the plane, regular, hexagonal model of benzene, on account of the number of coinci-

dent frequencies between the Raman effect and the infrared absorption, is not tenable, and most of these coincidences can be explained as being accidental. This eliminates one of the principal objections to the acceptance of a model which has a center of symmetry.

Symmetry

There are other considerations based on symmetry which will yield information regarding the constitution of benzene. The plane, regular, hexagonal molecule has the symmetry D_{6h} , while the Kekulé model has the symmetry D_{3h} and the triagonally puckered model has the symmetry D_{3d} . The total number of possible vibrations for all three models is 30. The molecule having the symmetry D_{6h} possesses ten non-degenerate vibrations, and ten twofold degenerate ones. Of these 20 vibrations four are allowable in infrared absorption and seven in the Raman effect. Of these seven vibrations, five are doubly degenerate and depolarized. All these vibrations are shown in Figures 17 and 18. The molecule with the symmetry D_{3h} possesses 14 Raman frequencies, of which ten are depolarized and four polarized. The molecule with the symmetry D_{3d} has nine fundamental Raman frequencies, five of which are depolarized and four polarized.

This then brings to the fore the basic question of what are the fundamental frequencies of benzene. If it is assumed that the plane model with the symmetry D_{6h} is the correct fundamental representation, then the frequencies active in the Raman effect are given in Table 34, together with

Table 34.—Fundamental Vibrations of Benzene and Benzene- d_6 .

Raman Effect			
$\Delta\bar{\nu}$	Benzene Figure	Degeneracy	Benzene- d_6 $\Delta\bar{\nu}$
606	18	2	577
849	18	2	661
992	17	—	945
1178	18	2	867
1596	18	2	1559
3047	18	2	2264
3062	17	—	2292
Infrared			
671	17	—	503
1037	18	2	831
1485	18	2	1331
3080	18	2	2294

the four infrared-active frequencies which are listed separately. In addition are depicted the equivalent Raman shifts for the corresponding deuterium derivative, benzene- d_6 . This does not, however, account for all the frequencies observed, some of which represent combinations and overtones which are shown in Table 35 as calculated and observed values.

These are useful in explaining most of the frequencies. The fundamentals listed do not include both shifts at $\Delta\bar{\nu}$ 1585 and 1606 but only one at $\Delta\bar{\nu}$ 1596, because the doubling of this shift is attributed to a resonance splitting resulting from the interaction of $\Delta\bar{\nu}$ 992 and 606 (≈ 1598) with $\Delta\bar{\nu}$ 1596. This idea receives confirmation in the fact that in the deuterium derivative

Table 35.—Combination Tones and Overtones in Benzene and Benzene- d_6 .

$\Delta\bar{\nu}$ (obs.)	Benzene $\Delta\bar{\nu}$ (calc.)	$\Delta\bar{\nu}$ (calc.)	Benzene- d_6	$\Delta\bar{\nu}$ (obs.)
404, 685, 802		—		337, 710
824, 1285	—	—		790, 976
1326	671 + 671 = 1342	503 + 503 = 1006		1000
1404	—	—		—
1449	606 + 849 = 1455	—		—
1693	$\begin{cases} 671 + 1037 = 1708 \\ 849 + 849 = 1698 \end{cases}$	$\begin{cases} 503 + 813 = 1316 \\ 661 + 661 = 1322 \end{cases}$		1327
1827	$\begin{cases} 777 + 1037 = 1814 \\ 1219 + 606 = 1825 \\ 992 + 849 = 1841 \end{cases}$	$\begin{cases} 752 + 813 = 1565 \\ 945 + 661 = 1606 \end{cases}$		1586
1936	—	—		—
2030	1178 + 849 = 2027	867 + 661 = 1528		1530
1988	992 + 992 = 1984	945 + 945 = 1890		1884
2128, 2293	—	—		—
2358	1178 + 1178 = 2356	—		—
2454	$\begin{cases} 1596 + 849 = 2445 \\ 1219 + 1219 = 2438 \end{cases}$	—		—
—	—	961 + 961 = 1922		1931
2543	1037 + 1485 = 2522	577 + 1559 = 2136		2128
2618, 2688, 2925	—	813 + 1333 = 2146		2145
—	—	—	2461, 2571, 2739	—
—	—	945 + 1559 = 2504		2510
2948	1485 + 1485 = 2970	961 + 1559 = 2520		—
3164	—	—		—
3187	1596 + 1596 = 3192	1559 + 1559 = 3118		3110
—	—	813 + 2294 = 3107		—
3467	—	—		—
3680	3062 + 606 = 3668	—		—
3916	3062 + 849 = 3911	945 + 503 = 1448		1457

the corresponding shift at $\Delta\bar{\nu}$ 1559 is single. This is as it should be, since a combination of $\Delta\bar{\nu}$ 945 and 577 would give $\Delta\bar{\nu}$ 1522, which is too far removed from $\Delta\bar{\nu}$ 1559 to produce resonance splitting.

The number of fundamental vibrations, the activity in the infrared and Raman spectra and the polarization of the Raman lines are not, therefore, in conflict with the acceptance of the plane, regular, hexagonal molecule of the D_{6h} symmetry. The application of the Teller product theorem also yields results consistent with this view. The conclusion may be reached, at least tentatively, that this model gives the best representation of the benzene molecule. The plane ring model has been assumed also by Klit and Langseth⁸¹⁷ and Lord and Andrews.⁹⁰⁸ The latter authors have analyzed the spectroscopic data for benzene to obtain a complete set of

vibrational frequencies. This analysis leads to a spectroscopic value of the entropy of gaseous benzene. The irregular changes in intensities of the Raman lines in passing from benzene to benzene- d_6 have been explained and at $\Delta\tilde{\nu}$ 993 in ethane.

The fundamental vibrations listed in Table 34, which are Raman active, may be divided roughly into four groups. In benzene $\Delta\tilde{\nu}$ 606 represents a carbon bending motion, arising from the elongation and narrowing of the hexagonal configuration. The frequency at $\Delta\tilde{\nu}$ 1596 represents the oscillation of two pairs of C—H groups on opposite sides of the ring toward and away from each other. It may be seen that this type of motion is roughly analogous to the ethylenic type of vibration. A hydrogen stretching vibration resulting from the vibration of the hydrogen atoms along valence bonds connecting them to the carbon atoms in the ring corresponds to $\Delta\tilde{\nu}$ 3047. A hydrogen bending motion is found in the vibrations of the hydrogen atoms perpendicular to the C—H bond yielding $\Delta\tilde{\nu}$ 1178. There are two vibrations which can be assigned to a type of ring motion. These are $\Delta\tilde{\nu}$ 992, corresponding to the symmetrical expansion and contraction of the ring wherein all the C—H groups move together outwardly or inwardly and in phase with one another. The shift at $\Delta\tilde{\nu}$ 3062 corresponds to a similar type of motion, but in this case the carbon and hydrogen atoms are moving simultaneously in opposite directions. The last two types of vibration are nondegenerate and correspond to the only two polarized lines. This leaves $\Delta\tilde{\nu}$ 849 as corresponding to the bending of the hydrogen ring caused by the motion of the hydrogen atoms perpendicular to the plane of the carbon ring.

Carbon Isotope Effect

The group of lines represented by $\Delta\tilde{\nu}$ 979, 984, 992, 999 and 1005 is of particular interest. These lines represent four satellites of the strong line at $\Delta\tilde{\nu}$ 992, since Howlett⁷⁶⁷ using high dispersion resolved the line at $\Delta\tilde{\nu}$ 992 into the five components named above. These lines represent essentially the rotational structure of the strong line. However, the shift at $\Delta\tilde{\nu}$ 984 has been attributed by Gerlach,⁵⁹⁶ Bhagavantam,¹⁶¹ Grassmann and Weiler,⁶⁴¹ Specchia and Scandurra¹⁵⁰⁰ and others to the presence of a carbon isotope of mass 13 in the benzene ring. Cheng, Hsueh and Wu⁸⁶⁷ have determined the relative intensities of $\Delta\tilde{\nu}$ 992 and 984, and find that the former shift is 16 times more intense than the latter which would, therefore, correspond to the proper intensity ratio if one carbon atom in the ring is isotopic. The theoretical displacement of the Raman shift from $\Delta\tilde{\nu}$ 992 due to C^{13} is $-\Delta\tilde{\nu}$ 6.3, in agreement with the observed value. The presence of this isotope in cyclopropane and the derivatives of benzene has been ascertained by these authors and by Bhagavantam,¹⁶¹ who has also come

to the conclusion that this isotope is present in cyclopropane and in ethane from an analysis of the fine structure of the shift at $\Delta\bar{\nu}$ 1188 in cyclopropane and at $\Delta\bar{\nu}$ 993 in ethane.

Bhagavantam and A. V. Rao have carefully investigated the Raman spectrum of benzene in the vapor and liquid phases or, in other words, as a function of the state of aggregation. In the vapor phase the experiments were carried out at approximately 180° C. under 15 atmospheres pressure. The Raman shifts at approximately $\Delta\bar{\nu}$ 606 and 992 in the liquid show no alteration in the vapor phase. The shift which occurs at $\Delta\bar{\nu}$ 3062 is augmented to $\Delta\bar{\nu}$ 3069 in the vapor, and at the same time the $\Delta\bar{\nu}$ 3047 shift is completely extinguished or very much weakened in the vapor. The latter effect also had been noticed previously by Sirkar¹⁴⁶⁹ but the $\Delta\bar{\nu}$ 3062 shift apparently remained constant, according to his observations. There are other important differences that will be discussed later. At low temperatures Epstein and Steiner⁵³⁵ have observed a decrease in these shifts amounting to a few wave numbers in going from above room temperature to - 20° C.

Wings

The extremely low frequency shifts in benzene and other compounds originally observed by Gross and Vuks^{664, 665, 666, 667, 668, 669} have been the subject of various interpretations. These generally occur at frequencies below $\Delta\bar{\nu}$ 100 and cannot be ascribed, therefore, to any fundamental vibrations of the molecules. Due to their close proximity to the incident radiation or the Rayleigh line, it is difficult to interpret these lines or bands, and extremely difficult from an experimental point of view to measure them with any degree of accuracy. It was originally supposed that the continuous spectrum associated with the incident radiation was composed of two parts: first a central zone, superposed on the Rayleigh ray, which increases in intensity with temperature, and secondly an exterior zone which does not increase in intensity with temperature. This behavior was interpreted as being in harmony with the view that this represents a Raman vibration spectrum rather than a rotational one. In the case of crystalline benzene there are two low-frequency Raman lines, according to Gross and Vuks,⁶⁶⁹ at $\Delta\bar{\nu}$ 62 and 104 instead of the continuous spectrum shown by the liquid in the region of the Rayleigh line. The continuous spectrum in this and other compounds in the liquid phase is presumed to arise from a broadening of the lines in the crystal, which become more diffuse and large with increased temperature and disappear at 250° C. The displacement in the liquid from the exciting radiation is attributed to intermolecular vibrations in the crystals which remain, although very deformed, in the quasi-crystalline liquid. Reference should be made in this connection to the discussion

of a somewhat similar effect which is treated in detail in that portion of the inorganic section (Part III) devoted to the Raman spectra of water and glasses.

The interpretation of the low-frequency shifts in the case of benzene and other similar compounds as a function of the vibrational spectra has not been entirely in agreement with the observations of Sirkar¹⁴⁶⁷ and Sirkar and Maiti.¹⁴⁸³ According to Sirkar and Maiti it has been found that the rotational wing in liquid benzene does not start with a maximum intensity in the center of the Rayleigh line, but that it starts with zero intensity at this point, and that its maximum intensity occurs at approximately 18 wave numbers from the Rayleigh line and subsequently diminishes. The diminution may extend as far as approximately 120 wave numbers. In the vapor phase both the position of the maximum and the breadth of the band are shifted to lower values. Sirkar¹⁴⁶⁷ has examined the intensity in the wing accompanying the Rayleigh line of benzene, dissolved in cyclohexane, and finds a diminution in intensity near the Rayleigh line and an increase near $\Delta\tilde{\nu}$ 50. The interpretation of these observations is that the wing cannot owe its origin to lattice vibrations; and the discrepancy between the intensities in the vapor and liquid phases can be explained by assuming that it originates partly in a rotational effect and partly in the fluctuation of the intermolecular field caused by non-periodic impacts of neighboring molecules on the scattering centers. Bhagavan-tam,¹⁶⁰ on the other hand, considers that the wings are due to hindered rotation and oscillation in quasi-crystalline groups. The difference between these points of view rests primarily on the premise that a quasi-orderly arrangement of the molecules may persist in the liquid phase and is complicated by the presence of a rotational effect. It is to be admitted that lattice vibrations do exist in the solid phase and that these become broadened on solution. Sirkar and his co-workers^{1472, 1473, 1478, 1480, 1482, 1484} believe in general that the wings of less than $\Delta\tilde{\nu}$ 70 do not owe their origin to a quasi-crystalline state but to the combination of effects named above. Bapayya⁸⁸ has reported the measurements of the wing intensity in benzene at various temperatures up to 210° C. and concludes that there is no increase in intensity of the wing between $\Delta\tilde{\nu}$ 20 and 50, and that the extent of the wing does not alter, in agreement with the observations of Gross and Vuks⁶⁶⁹ on diphenyl ether. During the last year Venkateswaran (Raman Jubilee volume) and Gross and Vuks have investigated low-frequency shifts in other compounds. The former interprets them as arising partly from translational and partly from rotational oscillations of the molecule in a definite phase relationship with each other in the crystal lattice. The latter author points out that the polarization data indicating depolarization is no argument in favor of rotation since the depolarization of every

line in some crystals depends on their orientation, and that in the liquid phase, with random orientation, the lines should be depolarized.

Monosubstituted Benzenes

In an extensive series of publications Kohlrausch and his co-workers (note compound index for complete list) Reitz and others^{1372, 1373, 1374} have determined the effect of substitution on benzene. Murray and Andrews^{1151, 1152} and many others (note bibliography) have also investigated monosubstituted and polysubstituted benzenes. In Table 36 are

Table 36.—Characteristic Frequencies of Benzene and its Monosubstitution Derivatives.

Substance	$\Delta\nu$					
C_6H_6	605(3)	992(10)	1178(3)	1605(1)	3057(1)	
Hydrocarbon derivatives				1584(3)	3060(5)	
$C_6H_5CH_3$	622(2)	1022(8)	1029(1)	1154(1)	1209(3)	1604(2)
$C_6H_5CH_2CH_3$	620(2)	1033(8)	1029(1)	1157(3)	1203(2)	1604(5)
$C_6H_5CH=CH_2$	623(5)	999(7)	1029(1)	1154(1)	1205(8)	1601(10)
$C_6H_5=CH$	623(5)	1000(7)	1029(1)	1158(1)	1195(8)	1601(10)
$C_6H_5CH_2CH=CH_2$	623(5)	1000(7)	1029(1)	1158(1)	1205(5)	1599(10)
$C_6H_5CH=CHCH_3$	621(5)	999(8)	1031(1)	1149(5)	1210(8)	1599(10)
$C_6H_5-CH-CH_2$	623(5)	999(7)	1026(1)	1156(1)	1220(8)	1604(8)
$C_6H_5-CH_2-C \equiv CH$	623(1)	1000(8)	1033(1)	1158(1)	1200(5)	1601(7)
$C_6H_5C_6H_5$	611(1)	994(5)	1022(2)	1146(1)	1191(1)	1589(3)
$C_6H_5CH_2C_6H_5$	623(4)	1012(8)	1037(4)	1145(2)	1175(4)	1593(6)
$C_6H_5CH_2CH_2C_6H_5$	619(3)	1002(10)	1032(4)	1153(2)	1200(4)	1600(5)
$C_6H_5CH=CHC_6H_5$	620(3)	1004(10)			1188(15)	1590(15)
<i>(trans)</i> $C_6H_5CH=CHC_6H_5$	615(2)	1000(10)	1027(2)	1150(4)	1190(4)	1596(10)
<i>(cis)</i> $C_6H_5C \equiv C_6H_5$	621(2)	997(5)	1028(1)	1140(15)	1174(2)	1590(20)
				1155(2)	1188(2)	
Benzyl compounds						
$C_6H_5CH_2Cl$	619(4)	1000(3)	1034(1)	1159(1)	1211(1)	1600(1)
$C_6H_5CH_2NH_2$	622(4)	1001(8)	1028(2)	1156(4)	1201(4)	1606(4)
$C_6H_5CH_2OH$	610(0)	1000(3)			1196(1)	1594(2)
$C_6H_5CH_2NO_2$	623(4)	1005(8)	1029(3)	1160(2)	1197(3)	1596(5)
$C_6H_5CH_2CN$	620(2)	1007(4)	1030(1)		1187(2)	1597(2)
Various derivatives						
C_6H_5OH	614(2)	1002(5)	1024(3)	1170(3)		1598(3)
C_6H_5CHO	615(3)	1001(8)	1023(1)	1164(5)	1203(6)	1597(10)
C_6H_5COCl	615(3)	1003(6)	1028(2)	1168(2)	1206(3)	1592(6)
$C_6H_5COOCH_3$	613(3)	1000(7)	1023(1)	1160(1)		1602(10)
$C_6H_5COCH_3$	613(3)	999(5)	1025(3)	1155(1)		1597(6)
C_6H_5Cl	615(6)	1001(10)	1021(6)	1156(4)		1581(6)
C_6H_5Br	608(1)	1000(4)	1022(2)	1159(1)		1576(2)
C_6H_5I	610(3)	998(7)	1012(4)	1158(2)		1568(5)
$C_6H_5NH_2$	617(3)	996(10)	1029(5)	1147(3)		1601(10)
$C_6H_5NHC_6H_5$	620(2)	1000(12)	1030(5)		1181(4)	1603(12)
$C_6H_5NO_2$	604(1)	1000(3)				1587(4)
C_6H_5CN	619(1)	998(5)		1175(2)	1190(3)	1595(4)

given the principal lines from benzene and its monosubstitution derivatives. These data are taken from Bourguet²⁶⁵ and are partly based upon observations of Dadiou, Pongratz, and Kohlrausch, and of Kohlrausch and Pongratz.

Disubstituted Benzenes

The effect of disubstitution in benzene is illustrated in Figures 36, 37 and 38, which illustrate the behavior of substituted chlorobenzenes containing different substituent groups.⁸⁶¹ Figure 36 represents the effect of *ortho* substitution, Figure 37 *meta* substitution, and Figure 38 *para* substitution. Considering first Figure 38, it is quite evident that there are at least seven frequencies which remain reasonably constant throughout all the compounds of benzene and its monosubstitution products. These are frequencies which are dependent upon the structural features of either the ring or the ring double bond. In these cases where a double bond occurs external to the ring the shifts characteristic of the ring double bond

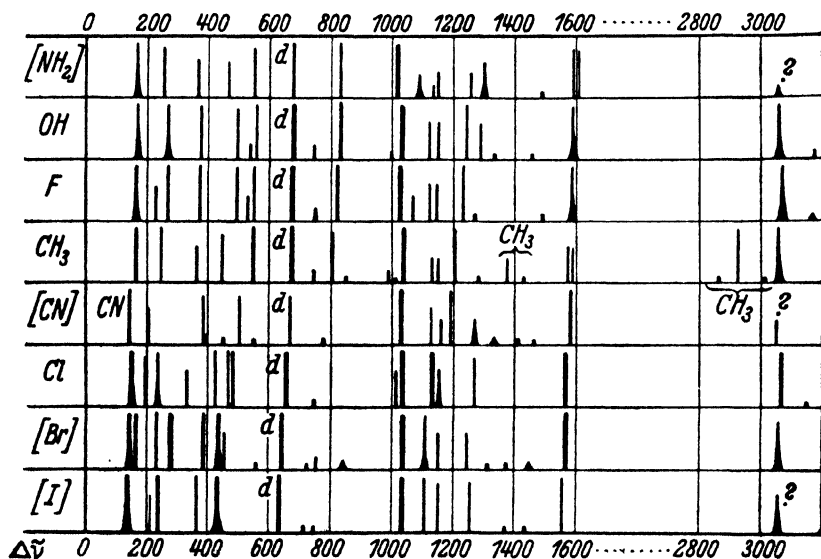


FIGURE 36. Raman Spectra of *Ortho*-substituted Benzene (after Kohlrausch and Pongratz).

alone are given. The C—H oscillation varies from approximately $\Delta\bar{\nu}$ 3047 to 3070 depending on the nature of the substituent group. It is noticeable that there is a reinforcement of the intensity of the C=C shift when there is a double bond external to the ring. This shift remains constant within 15 wave numbers, irrespective of the nature of the hydrocarbon substituent group. If, however, the substituent group is not a hydrocarbon radical but some other derivative, there is a greater alteration in the C=C frequency. This is particularly notable in the case of the halogens, where there is a progressive decrease in the frequency with the increase in molecular

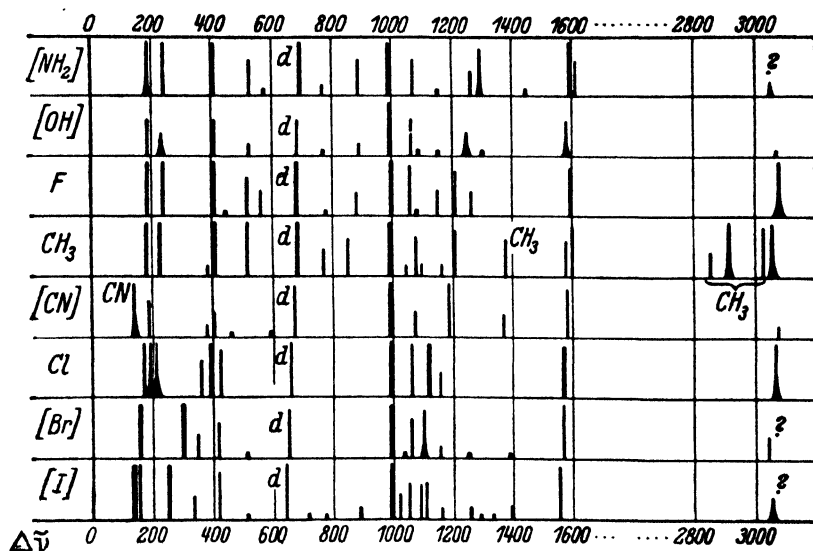


FIGURE 37. Raman Spectra of *Meta*-substituted Benzene (after Kohlrausch and Pongratz).

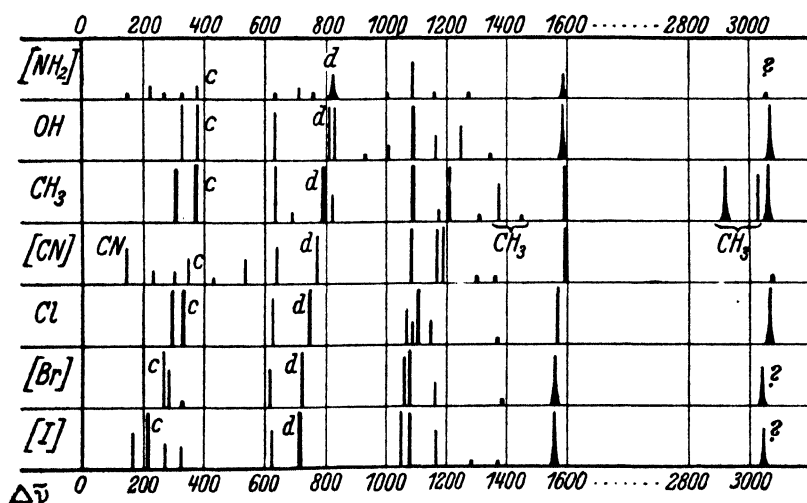


FIGURE 38. Raman Spectra of *Para*-substituted Benzene (after Kohlrausch and Pongratz).

weight of the halogen. There is likewise an effect on the C—H oscillation which decreases progressively from the $\Delta\tilde{\nu}$ 3066 to 3054 with the same halogen substitution. If, however, the halogen is removed from direct contact with the ring, as in benzyl chloride, the effect is much smaller. There is an appreciable reaction from conjugation with the carbonyl group. The net result, however, is that the effect of substitution on the ethylenic shift is less marked than in the case of the normal ethylenes, the cyclopentenes, or the cyclohexenes. In view of the conjugate nature of the ethylenic linkage in benzene it is of some importance that a substituent on one carbon atom in the aromatic nucleus must necessarily be attached to one ethylenic linkage and removed by one carbon from the next double bond. Nevertheless, this unsymmetrical arrangement results in only one strong Raman shift in this region. This would seem to give some weight to the dynamic conception of the nucleus in this case.

While it has been observed that the substitution of a methyl group in the aliphatic ethylenes and in cyclopentene and cyclohexene markedly increased the ethylenic shift, the passage from benzene to toluene causes only a very slight modification. Similarly in going from the methyl derivatives of unsaturated compounds, including cyclopentene, to the aldehyde derivative there is a marked decrease in the ethylenic shift. Progressing from toluene to benzaldehyde, however, the decrease is only about one-third of that observed in the other compounds. On the other hand, a similar progression of the carbonyl derivatives indicates that the esters of the aliphatic unsaturates and of cyclopentene have the largest carbonyl shifts and the aldehydes the least. By comparing methyl benzoate with benzaldehyde one observes a change in $\Delta\tilde{\nu}$ 1647 to 1689. This, therefore, is in the opposite direction from the frequency changes observed with the other compounds and is compatible with the classic effect of phenyl groups as contrasted with the alkyl radicals.

Polysubstituted Benzenes

In the disubstituted aromatics there are definite progressive changes in the Raman spectra depending on the substituent groups and the position of substitution. Kohlrausch and Pongratz have indicated some of these in the figures cited. It is particularly noticeable in the differences in *para*-substituted chlorobenzene as compared with the *ortho* and *meta* derivatives. In the substituted xylenes the frequency of the linear C—H shift increased from $\Delta\tilde{\nu}$ 3047 in *o*-xylene to $\Delta\tilde{\nu}$ 3070 in *o*-chlorotoluene. Kohlrausch and Pongratz⁸⁰⁰ give the frequency of aliphatic C—H binding in the series from toluene to pentamethylbenzene as being $\Delta\tilde{\nu}$ 1378(6), 1445(3), 2728(1), 2862(4), 2916(8), 3019(4). The effect of multiple substitution on the double-bond linkage is shown in Table 37, taken from

Table 37.—The Changes in the C=C Shift as a Function of Substitution in Polysubstituted Benzene.

Substance	Position of Substituent Groups	$\Delta\bar{\nu}$	
		X = Cl	X = CH ₃
C ₆ H ₆			1584(3)
C ₆ H ₅ X	1	1580(7)	1580(1)
	1, 2	1572(8)	1584(1)
C ₆ H ₄ X ₂	1, 3	1572(8)	1590(1)
	1, 4	1572(7)	1575(1)
	1, 2, 4	1564(8)	1567(4)
C ₆ H ₃ X ₃	1, 3, 5	1563(6)	1604(6)
	1, 2, 3	1554(2)	
	1, 2, 4, 5	1563(5)	1560(4)
C ₆ H ₂ X ₄	1, 2, 3, 5	1558(6)	1572(3)
	1, 2, 3, 4	1552(8)	1614(7)
C ₆ HX ₅	1, 2, 3, 4, 5	1553(5)	1572(3)
C ₆ X ₆	1, 2, 3, 4, 5, 6	1503(2)	1565(1)

data of Kohlrausch.⁸²⁶ The shifts in the entire spectra as a result of multiple substitution are shown in Figure 39, which gives the spectra of the polysubstituted chlorobenzenes.⁴⁴⁹

The changes in the spectra of benzene with progressive halogen substitution have been painstakingly investigated by Murray and Andrews.¹¹⁵²

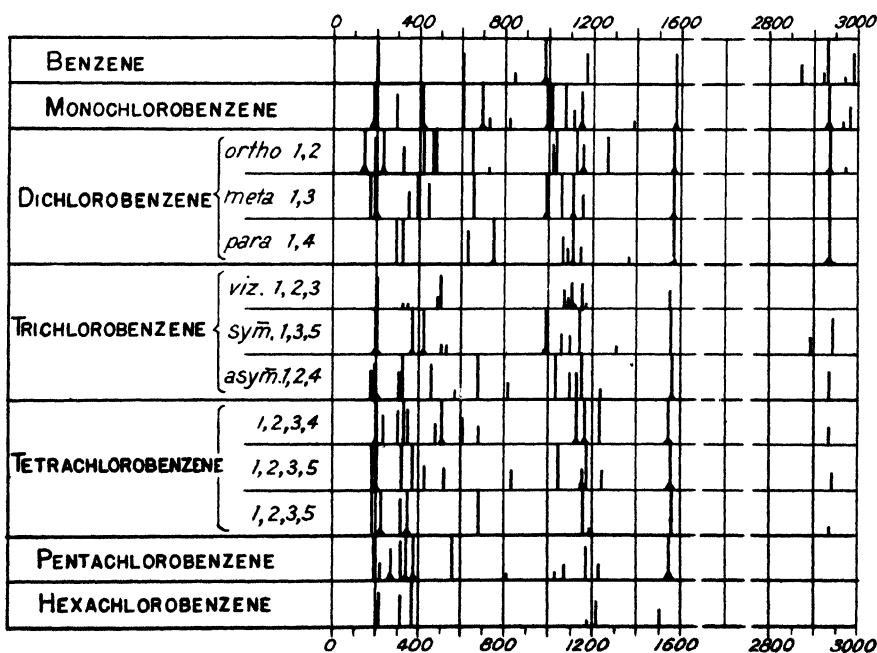


FIGURE 39. The Raman Spectra of Polysubstituted Chlorobenzenes (after Dadiou, Kohlrausch and Pongratz).

These authors observed new lines not observed by Dadiou, Kohlrausch, and Pongratz and have confirmed most of their observations. In particular they have found multiple lines in the $\Delta\tilde{\nu}$ 1600 region, most of which were not previously observed and are rather weak. In all the halogen derivatives very strong frequencies are noted between $\Delta\tilde{\nu}$ 200 and 400. The Raman spectrum of fluorobenzene resembles the spectra of the heavier monohalogen derivatives of benzene, but shows a certain marked difference. It is very similar to the spectrum of toluene, whose side-chain has approximately the same mass as fluorine. Between $\Delta\tilde{\nu}$ 1000 and 1200 the fluorobenzene spectrum is very different from the other halogen derivatives.

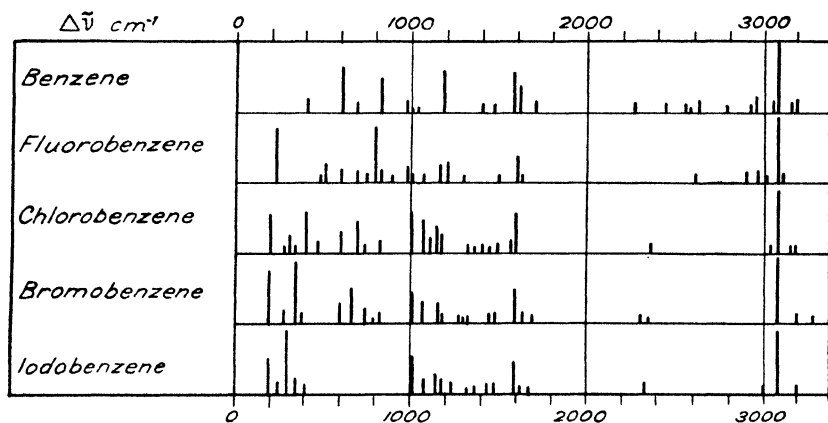


FIGURE 40. Raman Spectra of Halogen-substituted Benzenes (after Andrews).

This is indicated in Figure 40, which shows the effect of different halogen substitution. The frequencies indicated between $\Delta\tilde{\nu}$ 2200 and 2600 are stronger in the figure, in order to indicate them, than actually observed.

Chelation or Hydrogen Bonding

Chelation or hydrogen bonding is the result of the interaction of two adjacent radicals in such a fashion that neither behaves quite normally. This differs from keto-enol tautomerism in degree rather than in nature. In the latter case there is an actual migration of an atom of one radical to another and both compounds are isolable. In hydrogen bonding there is no oscillation from one radical to another but a coupling of the atom of one radical to an adjacent one under such conditions that the net result is a modification of the characteristics of both radicals. This results in what is generally termed a resonance hybrid, which means that there is an oscillation of one form to another, the statistical result being something of

a compromise between the two. The possibility of resonance has been indicated in the discussion of the structure of benzene and other compounds previously mentioned. Chelation or hydrogen bonding obviously refers to the interaction of a hydrogen atom with other groups. While it has been stated that as a general rule these compounds cannot be isolated, nevertheless in the case of some oximes Blatt has been able to show a considerable difference in the chemical and physical properties of pairs of isomers, one of which is hydrogen-bonded and the other is not.

This effect has been discussed as an explanation of the spectra of dibasic acids, alcohols and amines, but on the whole, it has been investigated primarily from the point of view of infrared absorption. There is no *a priori* reason why this should be so except that this effect was observed first by this means of approach and that it lends itself more easily to a quantitative method. There is no attempt in this discussion to present the infrared absorption results in their chronological order from the infrared point of view, except to mention that Wulf and Liddel were among the first to determine the actual infrared absorption of compounds of this type and to discuss their significance from an organic and theoretical point of view in collaboration with Hilbert and Hendricks.⁷²¹ Likewise it may be mentioned that Rodebush early postulated the existence of hydrogen bonding, and more recently with Buswell, has investigated the effect of hydrogen bonding by means of infrared absorption on hydroxyl groups.³⁰⁴ This has been discussed also by Freymann and her co-workers particularly in reference to amines, which will be discussed later under this heading. Reference should be made also to Gordy^{633, 634} for his work on solutions, and to the extensive publications, for example,¹⁰¹ of Barnes and his co-workers, on infrared absorption in general.

From the point of view of Raman spectra, most of the work has been carried out by Bonino and Manzoni-Ansidei^{246, 247, 249} and by these same authors in collaboration with Bolla.²⁵⁵ These authors have investigated, for example, resorcinol diacetate and 4-acetylresorcinol. They indicate that in resorcinol diacetate the characteristic C=O frequency is found at $\Delta\bar{\nu}$ 1769, but that in 4-acetylresorcinol, for example, the only frequency in this region appears at $\Delta\bar{\nu}$ 1629. There is also an effect on the shifts which appears near $\Delta\bar{\nu}$ 1325. This analogy is carried also to a comparison with the spectrum of salicylaldehyde, 4-acetyl-1-resorcylyl allyl ether and other equivalent derivatives in which the frequency near $\Delta\bar{\nu}$ 1324 is presumed to be modified by hydrogen bonding. Acetophenone, 4-acetylresorcinol, 2,4-diacetylresorcinol and 2,4-diformylresorcinol have also been investigated. Unfortunately the entire emphasis has been placed upon possible variations in the frequencies near $\Delta\bar{\nu}$ 1320 and possibly $\Delta\bar{\nu}$ 1620, rather than on any modification of the O—H frequencies which would be more suscep-

tible to alteration, according to the infrared spectra, than would any carbonyl vibration. It would seem to be apparent²⁵⁵ that there is some modification in the carbonyl frequency as the result of *ortho*-, *meta*- or *para*-substitution in hydroxyacetophenone as compared with acetophenone itself. The latter compound and some of its derivatives have been studied in detail by Kahovec and Wagner (Raman Jubilee volume). Other evidence from the same publication has been revealed by Murti and Seshadri.

Chapter 16

The Raman Spectra of the Terpenes, Terpene Derivatives, Terpenoids, Polycyclic Compounds and Diphenyl and its Derivatives

Terpenes, Terpene Derivatives and Terpenoids

Perhaps one of the most fruitful applications of the Raman effect lies in the field of the terpenes. Many of their structures are as yet uncertain, and the mixtures found in practice may be extraordinarily complex. In general, their structures are, of course, allied to that of benzene and cyclohexene as shown in Figure 41. It can be seen by comparing the spectra of the last three compounds and their constitutional formulas, that there are very strong similarities. Limonene has an external double bond of the general formula $R_1R_2C=CH_2$, whose frequency shift is in the neighborhood of $\Delta\bar{\nu}$ 1650. Its internal double bond shift, $\Delta\bar{\nu}$ 1681, is similar to that of methylcyclohexene, $\Delta\bar{\nu}$ 1675. Carvomenthene likewise gives $\Delta\bar{\nu}$ 1681. Consequently the magnitudes of the frequency displacements in these compounds are compatible with their presumed structures.

Nevgi and Jatkar¹¹⁶⁶ have studied a series of terpenes to determine if there are any differences in the frequency shifts from terpenes identical except for optical activity. The results are indicated in Figure 42.

The abbreviated formulas for these compounds are given in the figure. All these terpenes contain double bonds; some of these double bonds, however, are within the ring and some without, and their position is not always identical. Δ^3 -Carene and Δ^4 -carene are identical except for the position of the double bond in the cyclohexene ring and its relation to the C_3 ring. The spectra, as far as the $C=C$ shift is concerned, are somewhat different, *d*- Δ^4 -carene giving $\Delta\bar{\nu}$ 1554, 1639 and 1670, as compared with $\Delta\bar{\nu}$ 1641 and 1683 for *d*- Δ^3 -carene. The *l*- Δ^3 -carene has $\Delta\bar{\nu}$ 1685 as the only observed frequency shift in this region. This is comparable with the ethylenic shift obtained from substituted cyclohexene. The other isomers containing a ring double bond give, however, a lower frequency shift, such as $\Delta\bar{\nu}$ 1642 for *d*- α -thujene and $\Delta\bar{\nu}$ 1657 for the *d*- and *l*- α -pinenes. Apparently when the bridge in the cyclohexene nucleus is so situated that it is close to the ring double bond, as in Δ^4 -carene and the pinenes, the $C=C$ frequency is reduced. If, however, it is more distantly removed as in Δ^3 -carene, the

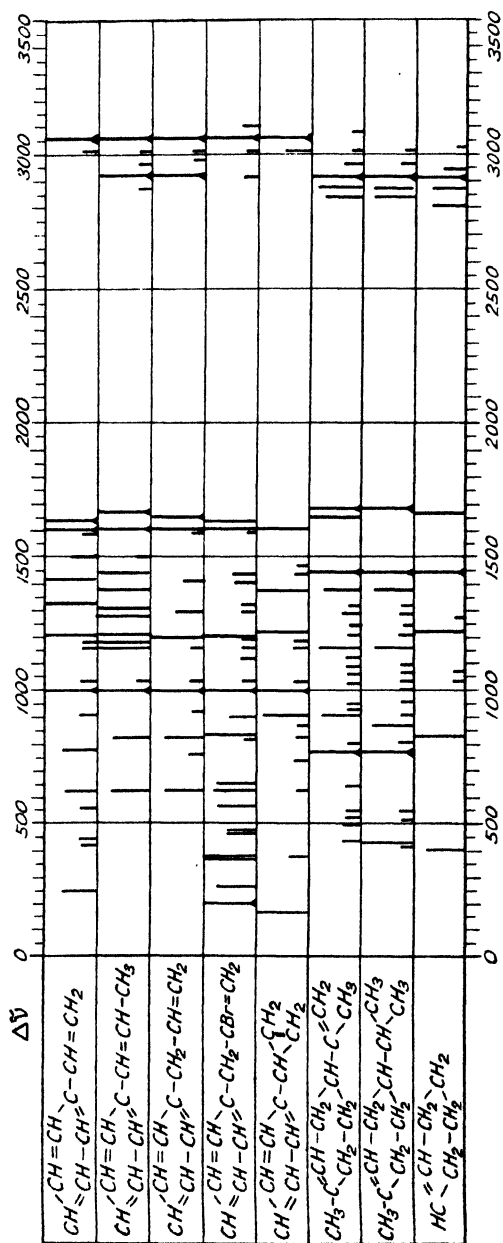
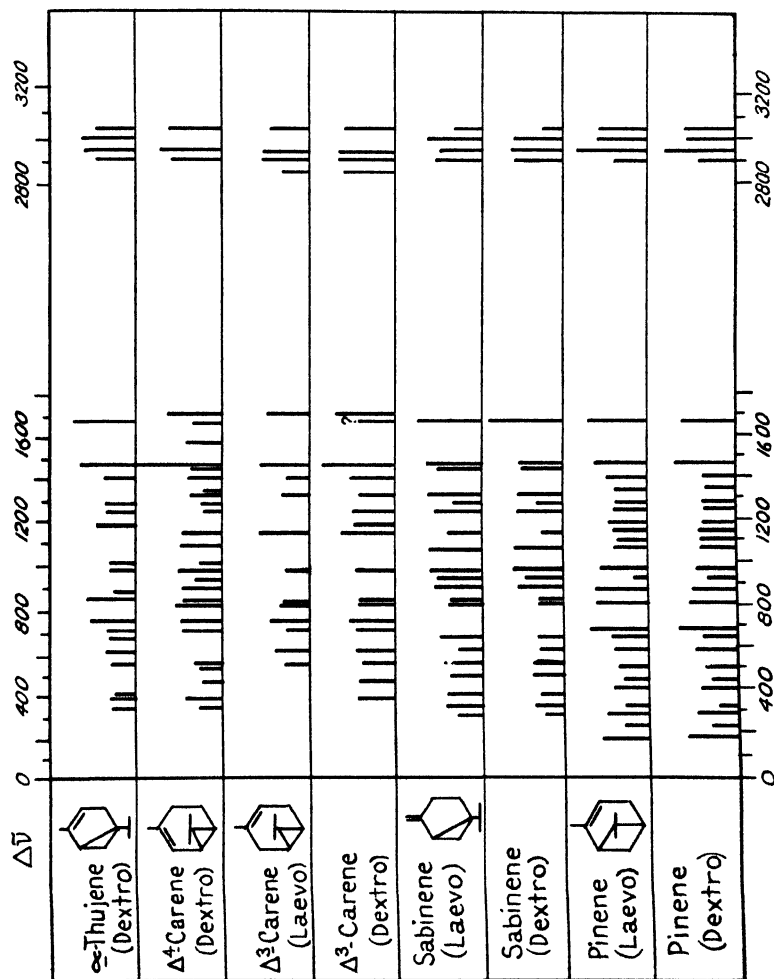


FIGURE 41. Raman Spectra of Benzene and of Some Cyclic Compounds Containing Internal and External Double Bonds (after Lespiau and Bourguet).

FIGURE 42.
Raman Spectra of Some
Polycyclic Terpenes (after
Nevgi and Jatkar).



normal cyclohexene shift is present. The two sabinenes give identical C=C shifts at $\Delta\bar{\nu}$ 1653, which is an approximately correct position for a compound of the type $R_1R_2C=CH_2$.

All these compounds show a shift near $\Delta\bar{\nu}$ 1440 characteristic of the CH_2 -group. (See Chapter 7.) The linear C—H oscillation occurs at $\Delta\bar{\nu}$ 3008 in the carenes and in the thujenes, at $\Delta\bar{\nu}$ 3030 in the pinenes, and at $\Delta\bar{\nu}$ 3046 in the sabinenes. While these shifts are given an intensity of 1 to 3 in these terpenes, it is to be noted that they are apparently absent or very much weakened in ordinary cyclohexene derivatives. The conclusion is that while these isomers differ one from another, particularly in the lower frequency region, and may thus be distinguished without too much difficulty, there is no apparent difference in intensity or magnitude between the *dextro*- and *levo*- forms of the same compound.

Hayashi⁷⁰⁹ has discussed the alkyl derivatives of cyclohexane and cyclohexene with particular reference to their Raman spectra in connection with the terpene derivatives. He observes that the methyl-, ethyl-, and isopropylidenecyclohexanes have $\Delta\bar{\nu}$ 1655, 1676, and 1674, respectively, and the substituted cyclohexenes have shifts close to that expected from multisubstituted ethylenes.^{706, 707}

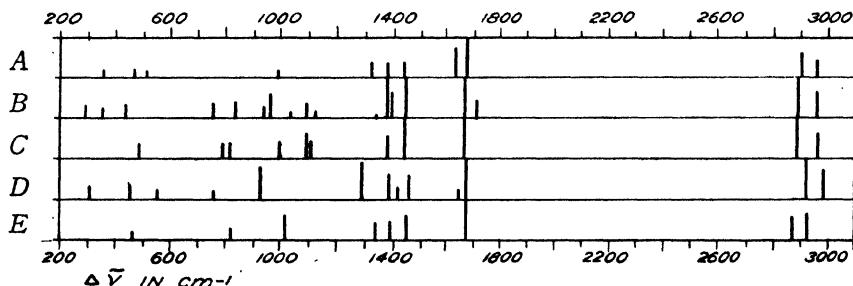


FIGURE 43. The Raman Spectra of Some Aliphatic Compounds Isomeric with Terpenes (after Bonino and Cella).

- | | |
|---------------------|--|
| A—Geranial (Citral) | $(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCHO$ |
| B—Citronellal | $CH_2=C(CH_3)(CH_2)_3CH(CH_3)CH_2CHO$ |
| C—Citronellol | $CH_2=C(CH_3)(CH_2)_3CH(CH_3)CH_2CH_2OH$ |
| D—Linalool | $(CH_3)_2C=CH(CH_2)_2C(CH_3)OH$ |
| E—Geraniol | $(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCH_2OH$ |

Bonino and Cella^{222, 226} have made a comprehensive investigation of the Raman effect of the terpenes and their derivatives. In Figure 43 are given the Raman spectra of a number of compounds which are not terpenes but are isomeric with them. These are geranial, geraniol, citronellol,

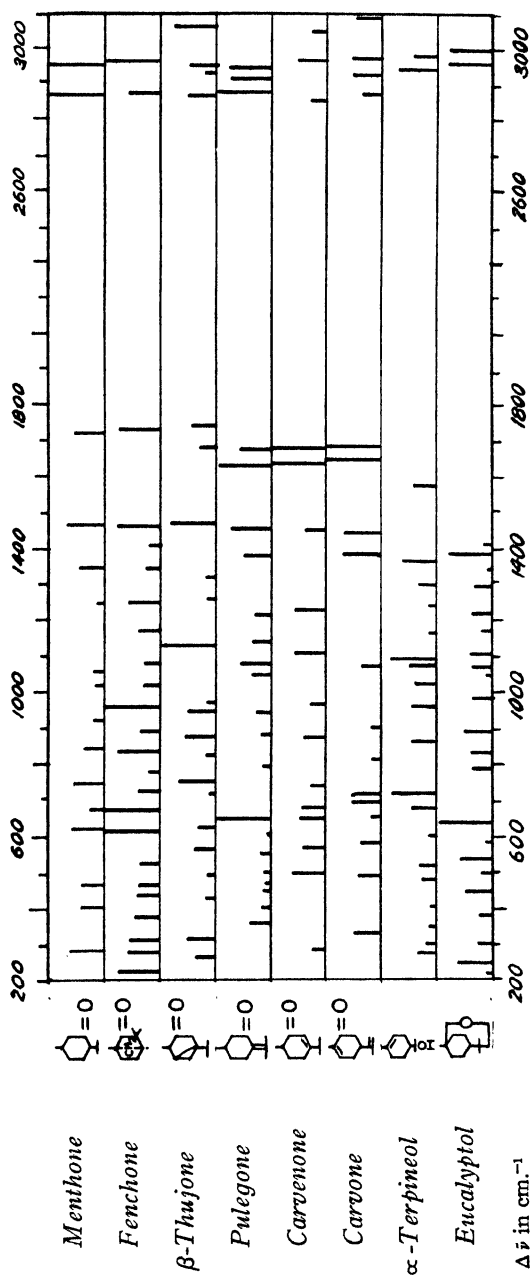


FIGURE 44. Raman Spectra of Some Terpene Derivatives (after Bonino and Cella).*

*  is the cyclohexane ring. In the unsaturated derivatives, the unsaturation is indicated by double bonds. A single bond extending from the ring represents a CH_3 group, while a $=\text{CH}_2$ is indicated by a double bond attached to the ring. $\perp$ represents $-\text{CH}(\text{CH}_3)_2$, $\_$ represents $-\text{C}(=\text{CH}_2)\text{CH}_3$. A straight line at the midpoint of which two other lines meet represents $\text{H}_3\text{C}-\text{C}-\text{CH}_3$.

citronellal, and linalool. These give for the corresponding C=C and C=O shifts respectively: geranial $\Delta\bar{\nu}$ 1640, 1681; geraniol $\Delta\bar{\nu}$ 1675; citronellol $\Delta\bar{\nu}$ 1675; citronellal 1675, 1719; and linalool $\Delta\bar{\nu}$ 1672, with 1646 very weak. In every case the double shift falls within the expected frequency region for a compound of that composition. The Raman spectra of a number of terpenes as determined by Bonino and Cella²²⁶ are given in Figure 44, which shows the influence of molecular constitution on the respective shifts.

On considering first the C—H shifts of these and other terpene compounds, it is noticed that pulegone contains a $-\text{C}=\text{C}\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ group but no $\text{>C}=\text{CH}_2$ group. The maximum frequency for the C—H line obtained in these compounds is, therefore, $\Delta\bar{\nu}$ 2951, which is in agreement with the precepts already enunciated. Carvenone possesses a ring $-\text{C}=\text{C}-$ group which may give rise to $\Delta\bar{\nu}$ 3049(1) for $\text{C} \leftrightarrow \text{H}$ (a type of shift which has not yet been observed in the substituted cycloolefins). This may also be present as $\Delta\bar{\nu}$ 3034(3) in *d*-pinene and as $\Delta\bar{\nu}$ 3082(2) in limonene. Carvone having a $\text{>C}=\text{CH}_2$ group yields $\Delta\bar{\nu}$ 3085(3). From the behavior of pulegone, menthone, and fenchone it is clear that the C=O cannot be responsible for any C—H frequency in excess of $\Delta\bar{\nu}$ 3000; neither does a C_3 ring structure as in sabinane ($\Delta\bar{\nu}$ 2964) nor the C_4 ring in pinane ($\Delta\bar{\nu}$ 2924) produce a frequency greater than $\Delta\bar{\nu}$ 3000. Sabinene, however, having both C_3 rings and $-\text{C}=\text{CH}_2$, shows $\Delta\bar{\nu}$ 3043(3) and 3076(3). β -Thujone, possessing no $-\text{C}=\text{C}-$ and only a C_3 ring in addition to the C=O group, gives rise to $\Delta\bar{\nu}$ 3067(4), according to Bonino and Cella.²²⁶ By employing Tables 14 and 15 and the known shifts for the alkylcyclohexanones and cyclohexenes, it is now possible to analyze the spectra of these terpenes with particular reference to the C=C and C=O shifts, and consequently determine if the observations are in accord with their constitution. This is shown in Table 38.

It is evident that there is a general agreement between the observed and expected frequencies. In determining the calculated frequencies the effects of conjugation or multiple double bonds and the type of substitution are included. In pulegone, for example, the C=C and C=O shifts were corrected for conjugation, and in carvone the two frequencies $\Delta\bar{\nu}$ 1638 and 1670 were also corrected. However, the extranuclear double bond under the influence of multiple bonding should yield $\Delta\bar{\nu}$ 1600 to 1610, which is not present. When it is remembered that this double bond is removed from the C=O by a distance of two carbon atoms, it is not unreasonable, in the light of the evidence so far presented, to assume that the effect of conjugation is negligible, and consequently the external C=C should

yield a normal shift corresponding to $R_1R_2C=CH_2(\Delta\bar{\nu} 1650)$. This is within the accuracy of these measurements and not distinguishable from the observed $\Delta\bar{\nu} 1646$. The same conditions were employed in calculating the shifts for the compounds given in Figure 43. If one double bond were

Table 38.—The Observed and Calculated C=C and C=O Shifts for Some Terpenes.

Compound	$\Delta\bar{\nu}$ Observed		$\Delta\bar{\nu}$ Calculated	
	C=C	C=O	C=C	C=O
Pulegone	1617	1673	1600	1670
Carvenone	1632	1673	1638	1670
β -Thujone		1688		1712
		1750		
Menthone		1714		1712
Fenchone		1731		1712
Terpineol	1675		1675	
Carvone	1646	1673	1638	1670
α -Pinene	1656		1675	
<i>l</i> -Limonene	1658		1650	
	1680		1675	
Sabinene	1650		1650	
Menthene	1673		1675	
Geranial	1647	1681	1640	1689
			1678	
Citronellal	1675	1719	1650	1720
Citronellol	1675		1650	
Linalool	1672		1678	
	1646		1640	
Geraniol	1675		1678	

far removed from any other in the molecule, it was considered to function as a separate unit and consequently yielded a shift the same as any other substituted ethylenic bond. If it were close to a C=O group the conjugation was considered effective. In citronellal conjugation was ignored. Geranial should yield $\Delta\bar{\nu} 1640$ (conjugate C=C) and $\Delta\bar{\nu} 1689$ (conjugate C=O) and a shift of conjugate type $R_1R_2C-CHR_3$ ($\Delta\bar{\nu} 1678$). The latter shift, however, falls so close to the observed frequency at $\Delta\bar{\nu} 1681$ that its presence is indeterminate. In geraniol and linalool the conjugation is ignored for the reasons already given.

The net result of this is that, with the exception of β -thujone, perhaps α -pinene, and the C=C shift for citronellal and citronellol, the calculated results are in rough accord with experimental observations. The limitations of this procedure will be referred to shortly.

These conclusions are not in agreement with Bonino and Cella, who discuss a reversed C=C frequency for carvenone, carvone, pulegone, and geranial. The lower frequencies near $\Delta\bar{\nu} 1650$ are ascribed to C=O instead of C=C, and the larger frequency shift ($\Delta\bar{\nu} 1675$) to C=C instead of C=O. This does not seem so logical or so compatible with the observations on the

terpenes and other compounds as the explanation which is given. These

authors have calculated the H—H angle in the $\text{—C=C}\begin{matrix} \nearrow \text{H} \\ \searrow \text{H} \end{matrix}$ groups in these

compounds as ranging from 104° in sabinane to 141° in carvenone. The force and deformation constants for the C—H linkage and the characteristic low frequency shifts in the terpene derivatives were determined. Many of the frequencies between $\Delta\bar{\nu}$ 1045 and 1450 have been accounted for on the basis of combination or rotational frequencies.

The differences in the Raman spectra of simple monocyclic terpenes possessing internal and external double bonds, and terpenes without double bonds are indicated in Figure 45, taken from the data of Dupont, Daure, Allard, and Levy.⁵⁰¹ These and other terpenes have been investigated by Daure,^{461, 462} Dulou,⁴⁹² Dupont, Daure, and Allard,⁴⁹⁷ Dupont, Daure, Allard, and Levy,^{498, 499, 500} Dupont, Daure and Levy,⁵⁰² Dupont and Gachard,⁵⁰⁸ Dupont and Joffre,⁵⁰⁹ Dupont, Levy and Marot,⁵¹⁰ Dupont and Dulou,⁵⁰⁵ Tabuteau,¹⁵³⁰ Venkateswaran and Bhagavantam.¹⁶⁴³ Attention is called especially to the excellent survey of Angus (Raman Jubilee volume) of the terpenes and their derivatives. Terpene mixtures have been analyzed by Dupont, Daure, Allard, and Levy,⁵⁰¹ and others. Bonichon,^{200, 201} after investigating a large number of alcohol and ester derivatives of the terpenes, concluded that there are enough distinguishing lines to differentiate the esters of a given terpene from one another and to determine the composition of mixtures of such closely allied compounds as the spatial isomers borneol and isoborneol. The analysis of the essence of terpenes, *Pinus longifolia*, by Raman spectra leads to the conclusion that there are present two forms of carene, namely, Δ^3 -carene and β -carene.⁴²⁸ The distillation of oil of indienne likewise has been followed and shows the presence of pinene, β -pinene, and Δ^3 -carene in successive distillates. Pinane and nopinane give identical Raman frequencies. Camphene yields $\Delta\bar{\nu}$ 1672 for the double bond, which is practically identical with that observed from β -pinene. There are, however, other lines which enable this compound to be distinguished from the pinenes. Tabuteau¹⁵³⁰ has fractionated the essence of citronel of Java, and has found pinene, β -pinene, limonene and other terpenes in the distillate. Dupont and Gachard⁵⁰⁸ have investigated a number of the camphenes and other terpenes and the composition of complex mixtures and have noted a change in constitution on hydrogenation.^{503, 508} This combination chemical and Raman spectra method has also been followed by Dupont, Levy, and Marot,⁵¹⁰ who studied the dehydration products of the terpinenes and terpeneol. The action of heat on some terpenes has been investigated by Dupont and Dulou.⁵⁰⁵

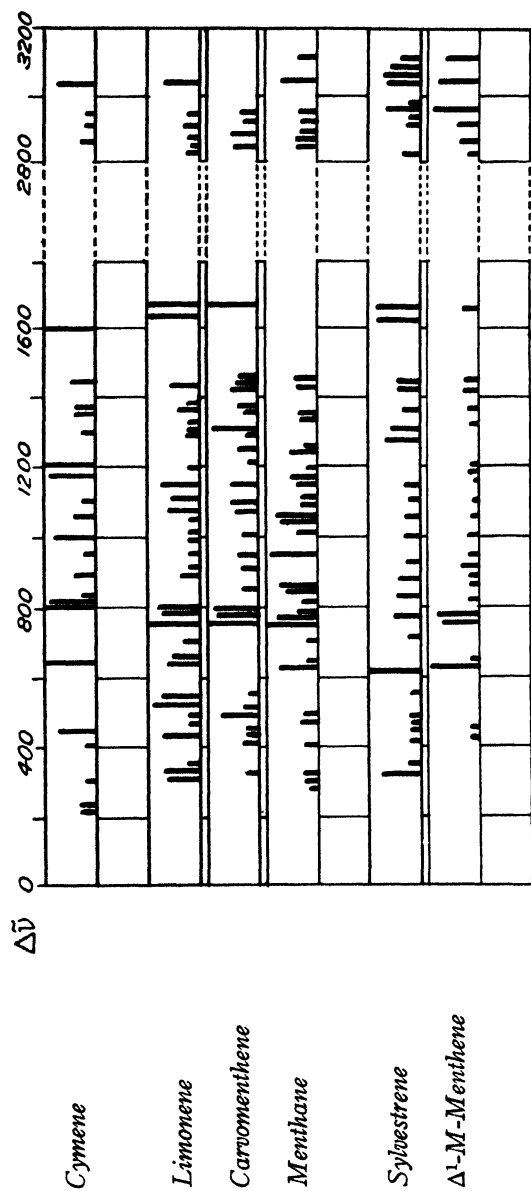


FIGURE 45. Raman Spectra of Some Simple Terpenes (after Dupont, Daure, Allard and Levy).

The pyrolysis produced a mixture of terpenes of a new type, given the name pyronenes. These show $\Delta\bar{\nu}$ 1596 and 1657 for the double-bond linkage and to them are attributed the formulas:



Thosar and Singh¹⁵⁶⁸ have investigated the *dextro*, *levo* and racemic forms of borneol and camphor. These results indicate that, from the Raman spectra point of view, the *dextro*- and *levo*- forms are identical, thus confirming Pasteur's law of molecular dissymmetry. The most intense shifts are those associated with the C—H vibration, although there is an intense line near $\Delta\bar{\nu}$ 650 which is ascribed to the neopentyl group vibration. In no case is a frequency corresponding to a carbonyl linkage observed. Singh and Misra¹⁴⁴⁸ have studied the *dextro* and *levo* camphoric acids and camphoric anhydrides. Their results also lead to the conclusion that in the *dextro*- and *levo*-compounds, the number, position, and intensities of the Raman lines are identical. Likewise, the most intense lines are due to the C—H oscillation, with a sharp line in the region of $\Delta\bar{\nu}$ 705 in camphoric acid and 607 in the anhydride ascribed to the neopentyl group. In neither the acid nor the anhydride is any frequency corresponding to C=O observed. This would seem to be one of the most significant features of the results, the explanation of which is yet to be forthcoming. On the other hand Bonino and Manzoni-Ansidei²³⁸ have observed for camphoric aldehyde two frequencies in the double bond region, $\Delta\bar{\nu}$ 1640(2) and 1716(1) and in camphor, $\Delta\bar{\nu}$ 1734(1). It is their contention, therefore, that camphoric aldehyde may exist in two tautomeric forms, one corresponding to the classic designation and the other to hydroxymethylene camphor, which would account for the simultaneous occurrence of the ethylenic and the carbonyl double bond.

Dextro- and *levo*- α -pinene have been studied by Bonino and Manzoni-Ansidei, and alloöcimene, anethole, eugenol, isoeugenol, safrole and other terpenes by Desreux.⁴⁸⁰ The presence of a characteristic atomic group is indicated by the data. The Raman frequencies for eugenol and some of its derivatives have been determined by Briner, Susz and Perrottet,²⁸⁶ Briner, Nemitz and Perrottet and Susz and Perrottet.^{1518, 1519, 1520} The ozonides of eugenol do not possess the characteristics of unsaturated side chains.

A detailed consideration of the terpenes could be continued indefinitely. This field of investigation is still somewhat in its infancy. It has been given this much space since the problems presented are of the same type

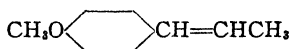
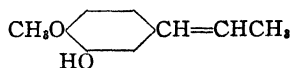
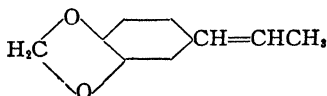
Table 38A.—Raman Spectra of Pinane and its Derivatives

Pinane			α -Pinene							β -Pinene			
1	2	3	4	5	6	7	8	9	10	11	12	13	14
		134(2)		123(2)	139			134(3)		134(3)			
		205(2)		213(4)	207	222(2)	217(2)	(208)(2)	210(1)	213(0)			
		260(2)		266(3)	258		273(4)	261(3)	265(3)	261(2)			
308(0)		309(1)		308(0)	307	278(4)	304(2)	306(2)	314(1)	306(0)			296(2)
		335(4)		335	335	309(2)		(333)(0)					327(2)
	366(1)	389(4)		392(2)	389	391(3)	386(2)	388(3)	395(1)	388(2)	391(1)		385(1)
401(0)				394	394								
	427(1)	423(4)		424	424			(426)(2)	429(1)	428(0)			
		465(4)		467	467	477(2)	472(2)	(465)(2)					462(2)
478(1)	472(2)	484(4)		478(1)	483			(488)(3)	480(2)	467(0)	480(2)	471(1)	488(2)
		568(1)		565(2)	565	573(4)	568(4)	564(4)	574(3)	564(2)			552(3)
		623(4)		619(1)	613	623(3)	618(3)	620(3)	626(2)	620(1)			
660(4)			644		623				648(5)	643(5)			639(4)
		669(5)		673(5)	668	672(7)	667(7)	667(6)	670(4)				
													712(2)
764(2)	752(5)	774(2)		778(2)	771	776(3)	771(3)	774(4)	779(3)	774(2)	778(2)	771(1)	761(2)
					780								
814(2)		823(4)	813		820			822(2)		816(0)			814(2)
858(3)	864(7)	848(3)	833	847(3)	845	840(5)	835(5)	844(5)	848(3)	844(2)	850(5)	845(3)	848(2)
								885(1)		878(0)	879(5)	879(3)	872(3)
		908(1)			889			905(3)	906(1)	904(1)			
					908								918
								930(1)		931(0)			931(2)
948(2)	957(4)	956(2)	951	953(2)	930			953(3)	953(3)	942(7)	937(3)		949(2)
					940								
					952								

as would be met in any complicated investigation. It is believed that the Raman spectra method has already made a genuine contribution in the delineation of the structure of the terpenes and in the identification of their constituents.

Attention has been confined thus far to some of the more favorable aspects of the general problem of Raman spectra applications to the terpenes. Angus (Raman Jubilee volume), however, has very ably and critically analyzed most of the present available data. He points out that a fair proportion of the reported Raman shifts—let alone intensities—have been inaccurately determined for the terpenes; that comparisons made between compounds by means of the ethylenic linkage are not justifiable when these compounds may contain a cyclobutane ring on the one hand or a cyclopropane ring on the other; that much of the experimental work lacks independent verification, and that measurements are frequently made on material for which there is no rigorous chemical or physical criterion of purity. This waif cannot be left on the doorstep of the proverbial "physical chemist." An example of results obtained by ten different observers on three different compounds are shown in Table 38A as compiled by Angus.

Before leaving entirely the question of the determination of the constitutional arrangements by means of Raman spectra based on the internal and external ethylenic linkages in benzene and its derivatives, there may be cited some work of Hayashi.^{706, 708} He determined the spectra of the following compounds:

*Anethole**Isoeugenol**Isosafrole*

The principal frequencies obtained for anethole are $\Delta\bar{\nu}$ 1591(9), 1644(10); for isosafrole $\Delta\bar{\nu}$ 1601(6), 1641(7); for isoeugenol $\Delta\bar{\nu}$ 1604(6), 1646(7). The question here is whether there may exist geometric isomers of these compounds as found in nature. The frequency of the ethylenic linkage external to the ring is approximately 10 wave numbers lower than that observed for the *cis*-form of compounds of the type $R_1CH=CHR_2$ ($\Delta\bar{\nu}$ 1658). Therefore, it was originally concluded that the *cis*-form of these compounds probably predominated, because the *trans*-form of the ordinary

disubstituted ethylenic linkage yields $\Delta\bar{\nu}$ 1673 (see Table 14). On closer inspection, however, it was observed that the ether and hydroxy groups even in the *para* position were not without their effect on the external ethylenic linkage. On comparing *trans*-isoallylbenzene $\Delta\bar{\nu}$ 1663, styrene $\Delta\bar{\nu}$ 1636, and *p*-methoxystyrene $\Delta\bar{\nu}$ 1620, a progressive decrease in the external ethylenic linkage is seen. The constitution of isosafrole, isoeugenol and anethole, as far as the side-chain is concerned, is more like that of isoallylbenzene. One would expect, therefore, a shift near $\Delta\bar{\nu}$ 1663, but, as just shown, the influence of the methoxyl group is to lower the side-chain frequency by approximately 15 wave numbers. This would diminish the expected $\Delta\bar{\nu}$ 1663 to 1648, which is approximately the observed frequency. It is concluded, therefore, that these compounds exist ordinarily in the *trans*-form rather than the *cis*. It may be remarked that the influence of the methoxy group in the *para* position is also noticeable by contrasting $\Delta\bar{\nu}$ 1700 for the C=O frequency in benzaldehyde with $\Delta\bar{\nu}$ 1687 observed in anisaldehyde. The conclusions, therefore, are compatible with the evidence. While this seems a perfectly straightforward deduction, it is somewhat in conflict in principle with the tenets which have been given in regard to the lack of influence of one group upon another if they are separated by any distance in the molecule.

Polycyclic Compounds

The Raman spectra of the polycyclic compounds are essentially an extrapolation of the observations on benzene and cyclohexane and their derivatives. While naphthalene has been investigated by a great many observers, its derivatives have been investigated primarily by Bonino,²⁰³ Bonino and Cella,^{221, 225} Gockel,⁶¹⁷ Hayashi,⁷⁰⁸ Mukerji,^{1142, 1143} and Ziemecki.¹⁷⁵⁸ Mukerji, and independently Bonino and Cella, Jatkari and others have studied Decalin, which is completely saturated naphthalene, and Tetralin. The latter has been investigated also by Venkateswaran.¹⁶²⁵ In Tetralin only one of the benzene rings has been saturated. These spectra have been compared to those of naphthalene and cyclohexane. There is a marked similarity among the entire group with the exception of the $\Delta\bar{\nu}$ 3046, (=C—H) which exists in naphthalene and Tetralin but not in Decalin. In Tetralin $\Delta\bar{\nu}$ 2940 occurs also. $\Delta\bar{\nu}$ 1037 appears weakly in Decalin and naphthalene and strongly in cyclohexane. $\Delta\bar{\nu}$ 699 in these observations corresponds to $\Delta\bar{\nu}$ 695 in cyclohexane. Many of the other shifts have the same significance which has been previously mentioned, such as, for example, $\Delta\bar{\nu}$ 1448 which corresponds to the transverse oscillation of the hydrogen. The C=C shifts at $\Delta\bar{\nu}$ 1602, according to Bonino and Cella, occur primarily in the Tetralin compound; $\Delta\bar{\nu}$ 1583 in Tetralin is absent in Decalin and is present as $\Delta\bar{\nu}$ 1573 in naphthalene.

This is slightly lower than the C=C linkage in benzene. In α -bromonaphthalene this is reduced still further and becomes approximately $\Delta\bar{\nu}$ 1550(5). There are other differences in these compounds in the very low frequency shifts. It has been pointed out by Mukerji and Venkateswaran that a similarity in the spectra of Tetralin and cyclohexane indicates that the compound is made up of a complete cyclohexane nucleus and one incomplete benzene nucleus. There are a number of wings which accompany some of the lines in Tetralin, particularly the Rayleigh line.

The most complete survey of the naphthalene derivatives has been made by Gockel.⁶¹⁷ This author studied the derivatives in the α - and β - (or 1,2-) positions. There is some modification in the spectra depending upon the ring position of the substituent. There is a very profound modification in the spectra of naphthalene on substitution. Many of the lines, however, such as $\Delta\bar{\nu}$ 515, 1012, 1146, 1385, and 1573, remain fairly constant. The influence of substitution of different groups is shown in Figure 46, which gives the middle and low Raman spectra of the naphthalene derivatives as a function of substitution. The upper half of the figure represents substitution in the α -position and the lower half represents substitution in the β -position.

Bonino²⁰⁹ concludes that naphthalene has the D_{2h} type of symmetry for the fundamental level of the molecule. This is based on known coincidences of the Raman lines with infrared absorption bands, and on the small number of Raman lines and infrared bands. The experimental data now available are considered inconsistent with a dissymmetrical structure such as proposed by Willstatter and Waser.

Kohlrausch⁸²⁹ has discussed the formula of naphthalene as a constitutional problem. Gross and Vuks^{667, 668} have examined the very low frequency shifts of naphthalene. Some of these occur as low as $\Delta\bar{\nu}$ 45, 73, and 109, and are accompanied by wings, which may not be connected with rotation as originally supposed, but with a slow oscillation characteristic of the crystal lattice.

Manzoni - Ansidei^{1021, 1022, 1025} has compared the spectra obtained from acenaphthene, 9,10-dihydroanthracene, phenanthrene and fluorene. Anthracene has a much simpler pattern than phenanthrene or the dihydro-derivative. In dihydroanthracene the C=C line noticed in anthracene itself has been shifted to $\Delta\bar{\nu}$ 1603 and there is some similarity to the spectra of *ortho*-disubstituted benzenes. The compound has a high degree of symmetry. Fluorene is less symmetrical than acenaphthene, the symmetry dropping to the C_{2v} type with a consequent large increase in the number of Raman lines.

Mention should be made of the results obtained by Manzoni-Ansidei and Lucchi¹⁰³⁰ from indene and 1-d-indene. Those lines present in indene-d

and not appearing in indene are $\Delta\bar{\nu}$ 800, 886, 1242, 2134, 2164, 2182 and 2293. All are very feeble, although $\Delta\bar{\nu}$ 1242 and 2293 are relatively the strongest. In indene there appear $\Delta\bar{\nu}$ 229, 392, 1225, and 3007 which are

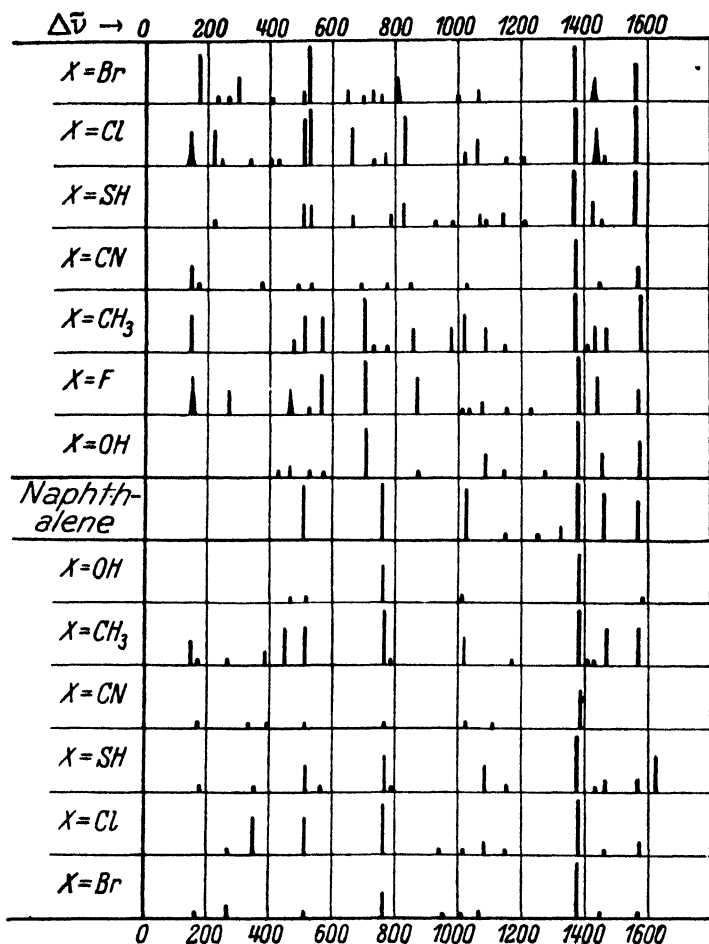


FIGURE 46. Partial Raman Spectra of Naphthalene and Some of its Derivatives (after Gockel).

not present in the deuterium compound. No special significance can be attached to these results except to note the expected lowering of one of the C—H frequency shifts to a value near $\Delta\bar{\nu}$ 2300 and possibly the transverse C—H vibration frequency reduction from near 1450 to 1242. In the double bond region there are two shifts $\Delta\bar{\nu}$ 1585(2) and 1606(8).

Diphenyl and its Derivatives

Diphenyl and its derivatives have been investigated principally by Bonino and Manzoni-Ansidei,²²⁹ although Dadiou* and Kohlrausch⁴¹⁹ and Wood^{1710, 1712} have also examined diphenyl itself. The hydrocarbon and halogen derivatives are confined to the observations of Bonino and Manzoni-Ansidei.

These compounds are considered here as an entity rather than with the benzene derivatives and the terpenes, because they are thus considered in organic chemistry. Diphenyl, of course, is simply a phenyl derivative of benzene from the standpoint of Raman spectra. The observed spectra are very close to the spectra of benzene and its derivatives and will not be discussed in detail. It can be remarked only that the C—H shift occurs as approximately $\Delta\tilde{\nu}$ 3067 and the C=C shift at $\Delta\tilde{\nu}$ 1597. It is to be expected that substitution of the methyl groups in the diphenyl ring produces increasing complexity of the Raman spectra as a function of the number of substitutions.

Chapter 17

The Raman Spectra of Sulfur and Metallo Compounds

Organic Sulfur Compounds

Quasi-organic sulfur compounds such as carbon disulfide and the inorganic thiocyanates are discussed in the inorganic section. The organic thioethers and mercaptans have been investigated by Bonino, Manzoni-Ansidei,²³⁰ Crigler,³⁹⁰ Dadieu, Pongratz, and Kohlrausch,^{445, 448} Kohlrausch and Koppl,⁸⁴⁰ Kohlrausch and Pongratz,⁸⁶⁰ Matossi and Aderhold,¹⁰³⁹ Meyer,¹⁰⁹¹ Gopala Pai,⁶²⁸ Thatte and Ganesan,^{1543, 1546} Venkateswaran,^{1612, 1615, 1619} and Wagner.¹⁶⁵⁸

The experimental observations by different workers are not in as close agreement as in other compounds. Nevertheless, it is quite apparent that the chain and C—H vibrations of the organic molecule are not seriously altered by the introduction of a sulfur atom. On the introduction of sulfur, however, new lines appear which are generally of strong intensity. This is the usual result when any heavy atom is introduced. There occur two inner vibrations, one characteristic of the C ↔ H linkage and one of the S ↔ H linkage. The latter appears near $\Delta\tilde{\nu}$ 2570, which is unique for a shift in this region, and hence this linkage is easily identified. The increased mass, as represented by the sulfur, would tend to reduce the S ↔ H frequency in comparison to the C ↔ H one. The reduction would be greater, as calculated, than is actually observed. Consequently there must be a comparative increase in the force constant of the S—H binding. The strongest C ↔ S shift falls near $\Delta\tilde{\nu}$ 645, although this depends somewhat on the amount of branching, and indicates that the force constant is slightly low after correcting for the mass influence. In Figure 47 are given the comparative spectra of the mercaptans, taken from the summary of Kohlrausch⁸²⁵ and based on the work of various observers.

Venkateswaran¹⁶¹² has indicated that the C—S shift in methyl mercaptan [$\Delta\tilde{\nu}$ 704(10)] decreases to $\Delta\tilde{\nu}$ 659(10) in ethyl mercaptan and to approximately $\Delta\tilde{\nu}$ 652 in the higher homologs. In the branched chain compounds this shift becomes first a doublet, and subsequently the lower frequency component of the doublet decreases in the magnitude of its shift with increased branching. The shift at $\Delta\tilde{\nu}$ 700 to 770, which persists in weakened form, is also characteristic of this linkage.

The thioethers contribute to the knowledge of the C—S shift. The stronger and more significant shifts of some of the thioethers are given in Table 39, based on the results of Venkateswaran^{1612, 1615} and of Thatte and Ganesan.¹⁵⁴⁶ The intensities recorded are difficult to correlate, as they are apparently given by authors on a somewhat different scale. The shifts pertaining more definitely to the oscillations involving the sulfur atom are italicized. In dimethyl sulfide there is a tendency for the shifts to pair. A comparison of this spectrum with that of diethyl ether shows

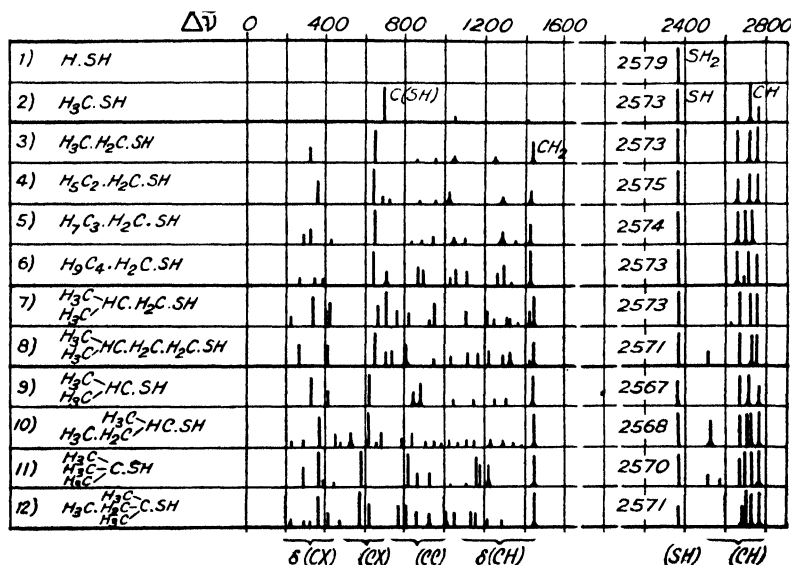


FIGURE 47. Raman Spectra of Some Mercaptans (after Kohlrausch).

that $\Delta\nu$ 441 and 845 in the ether correspond to $\Delta\nu$ 648 and 696 in the thioether, and that $\Delta\nu$ 928 and 1027 occurring in the ethyl ether correspond to $\Delta\nu$ 972 and 1052 in the sulfur compound.

In dipropyl sulfide most of the lower frequency shifts occur in pairs and are attributable to the influence of the sulfur. This tendency is continued in most of the higher sulfides. The strongest characteristic shifts of allyl sulfide are $\Delta\nu$ 616, 590, and 748. The $\Delta\nu$ 1206 and 1300, which are relatively weak in the other sulfides, are intensified in allyl sulfide. It is not entirely clear in the thio-acids just what shifts may be ascribed to the contribution of the sulfur. Presumably they are $\Delta\nu$ 638 and 818 in the two acids. From another point of view, however, these acids are very interesting. The carbonyl shift in thioglycollic acid is very weak and possibly represents a doublet, $\Delta\nu$ 1553 and 1707. In thioacetic acid, $\Delta\nu$ 1695 cor-

responds to the carbonyl shift and $\Delta\bar{\nu}$ 2568 corresponds to a S—H linkage. In general it may be assumed in agreement with Venkateswaran¹⁶¹⁵ that $\Delta\bar{\nu}$ 691 and 746 are more or less characteristic of the sulfur-to-carbon linkage. Other shifts such as $\Delta\bar{\nu}$ 284, 1033, 1252, and 1335 which are

Table 39.—The Raman Shifts from Some Thioethers and Thioacids

$\Delta\bar{\nu}$							
CH_3SCH_3	$\text{C}_2\text{H}_5\text{SC}_2\text{H}_5$	$\text{C}_4\text{H}_9\text{SC}_4\text{H}_9$	$[(\text{CH}_2)_3\text{CHCH}_2]_3\text{S}$	$\text{C}_6\text{H}_5\text{SC}_6\text{H}_5$	$[\text{CH}_2=\text{CHCH}_2]_3\text{S}$	CH_3COSH	CH_3OHCOSH
	318(1)	290(2) 378(1)			416(3) 590(5)	459(3) 638(5)	438(1)
691(6)	648(4) 696(3)	652(2)		655(3)	688(1)		
743(2)		730(2)	731(2) 814(2)	753(1) 794(1) 867(3) 892(3)	748(8) 753(8)	841(2)	818(4)
	972(2) 1052(1)	895(1) 1033(2)	950(2)	1054(3) 1102(3) 1298(3) 1417(4) 1454(6)	918(2) 1206(4) 1300(6) 1405(6) 1430(4)	1007(2)	914(2)
1424(1)	1245(1) 1453(3)	1445(2)	1458(2)			1426(1)	1409(2)
					1634(10)	1563(10) 1707(1)	
					2568(3)		
	2870(3) 2918(2) 2932(10)	2858(2) 2900(4) 2920(6)	2875(5)	2873(5) 2914(8) 2934(5) 2960(5)	2914(8) 2943(3) 2978(5)	2920(3)	
2912(8)							
2984(4)	2977(4)	2965(6)	2962(3)		3009(6) 3084(4)		2950(1)

variously ascribed to the linkage must be accepted with caution. While it is true that these make their appearance with increased complexity of the molecule, the appearance of any line with increased complexity is not a phenomenon solely confined to the thioethers. Most of these last-named shifts may be found as a first approximation in the hydrocarbons. Angus, Leckie and Williams assign $\Delta\bar{\nu}$ 1070 to the N—S bond.

There is another type of organic sulfur compound which has been somewhat investigated and is of considerable interest. This is the class of the polysulfides. They have been investigated by Venkateswaran,¹⁶¹⁵ Bonino and Manzoni-Ansidei,²³⁰ Gopala Pai,⁶²⁸ Meyer¹⁰⁹¹ and others. Results with some of the compounds investigated are in Table 40. The polysulfides as well as the monosulfides show a strong frequency near $\Delta\bar{\nu}$ 700. As noted in the case of sulfides, an increased complexity in the molecule results in an increased multiplicity of these sulfur frequencies. For

example, in dimethyl disulfide appears $\Delta\bar{\nu}$ 509; in diethyl disulfide this becomes $\Delta\bar{\nu}$ 508 and 526. This appears as $\Delta\bar{\nu}$ 513 in dimethyl trisulfide, but is completely absent in the ethyl derivatives. This is an anomalous behavior. There are frequencies in the polysulfides which are not far

Table 40.—The Raman Shifts from Polysulfides.

		$\Delta\bar{\nu}$		
$\text{C}_2\text{H}_5\text{S}$ $\text{C}_2\text{H}_5\text{S}$	CH_3S CH_3S		$\text{C}_2\text{H}_5\text{S}$ $\text{C}_2\text{H}_5\text{S}$	$\text{C}_2\text{H}_5\text{—S—S}$ $\text{C}_2\text{H}_5\text{—S—S}$
			157(3)	154(1)
197(3)	184(1)		203(3)	202(1)
	240(1)			
	282(1)			
332(2)			371(1)	
372(2)			439(2)	450(0)
	446(2)		487(4)	486(6)
508	489(3)			491(1)
526	513(3)			
644(5)		644(4)		644(3)
672(5)	700(5)	670(3)		665(1)
759(1)				
974(4)	958(1)	970(2)		965($\frac{1}{2}$)
1026(1)				
1055(3)		1050(2)		
	1152(1)			
	1225(0)	1199(1)		
1255(1)		1266(1)		1254($\frac{1}{2}$)
1353(2)	1312(0)			
1421(2)	1435(3)	1418(2)		1417(2)
1456(3)		1456(2)		1448(2)
2870(2)		1578(1)		2876(1)
2924(4)				2913(3)
				2931(4)
2971(4)	2985(2)	2970(0)		2969(2)
	3044(2)			

removed from those in sulfur. The $\Delta\bar{\nu}$ 433 and 470 in sulfur appear as $\Delta\bar{\nu}$ 446 and 489 in the trisulfide, and as $\Delta\bar{\nu}$ 450 and 486 in the tetrasulfide. It is doubtful what significance may be attached to this because the spectrum of sulfur is not determined in the form of S_2 or S_4 . Presumably the shift for the S—S bond is near $\Delta\bar{\nu}$ 500. This would give a calculated value of approximately $\Delta\bar{\nu}$ 725 for a S=S linkage. This apparently is absent. Consequently it is presumed that the sulfur in the polysulfides is bound together by a single homopolar linkage.

A comparison of the Raman spectra of diethyl sulfide, diethyl disulfide and diethyl trisulfide by Donzelot and Chaix⁴⁸⁹ shows that the frequencies at $\Delta\bar{\nu}$ 635, 655, 960, 1045 and 1150 relate to the C—S link and $\Delta\bar{\nu}$ 179 to the S—S in diethyl disulfide. The latter divides into $\Delta\bar{\nu}$ 151 and 204 in diethyl trisulfide. Médard and Dequillon¹⁰⁷³ likewise have investigated the dimethyl sulfur compounds containing one, two and three sulfur atoms.

The results for dimethyl sulfide differ appreciably from previous results. Those from the disulfide are characterized by a line at $\Delta\bar{\nu}$ 508 and those in the trisulfide by two lines at $\Delta\bar{\nu}$ 440 and 485, which is taken to indicate a branching of the sulfur chain rather than a linear molecule. In this connection, however, the compound was not pure so that a too definite conclusion is precarious. Phenyl mercaptan exhibits the usual S—H line at $\Delta\bar{\nu}$ 2568. Selenophenol has been investigated by Henri and Foster.⁷²⁴

The cyclic organic sulfur compounds which have been investigated are chiefly thiophene^{207, 231, 239, 240, 1028, 1361, 1611, 1643} and its derivatives, 2-methylthiophene, 2,5-dibromothiophene, and 2,3,5-trichlorothiophene. Bonino and Manzoni-Ansidei²³¹ obtained $\Delta\bar{\nu}$ 446(1), 602(3), 691(1), 743(2), 830(8), 1030(5), 1076(5), 1360(4), 1404(6), 3081(2), 3113(4) for thiophene. Especially characteristic are $\Delta\bar{\nu}$ 3113 and 3083 for the C $\leftrightarrow$ H and $\Delta\bar{\nu}$ 1404 to 1439 for C—H bending. The frequencies occurring at $\Delta\bar{\nu}$ 602(3) and 743(2) in thiophene become $\Delta\bar{\nu}$ 661(4) and 739(3) in 2-methylthiophene and $\Delta\bar{\nu}$ 654(4) and 704(1) in 2,5-dibromothiophene; they are reduced to a single frequency, $\Delta\bar{\nu}$ 683, in the trichloro- compound. The absence of a line corresponding to a classic C=C oscillation will be discussed later. It may be stated, however, that there are two frequencies, one at $\Delta\bar{\nu}$ 1360 and the other at $\Delta\bar{\nu}$ 1377 in both thiophene and methyl thiophene which are almost completely polarized. In addition there are two other shifts at $\Delta\bar{\nu}$ 1404 and 1439 respectively in these two compounds which are almost completely polarized. The other vibrations which are nearly completely polarized are $\Delta\bar{\nu}$ 830, 1076, and 3114 which, therefore, must necessarily correspond to a symmetrical type of vibration. There are other lines for thiophene than those indicated above, which are very weak.

There is another type of organic compound containing sulfur, which however may possess no C—S linkage. In this group are the alkyl esters of sulfuric acid, the alkyl sulfinates. Dimethyl and diethyl sulfates have been investigated by Milone¹¹⁰³ and Médard and Marchand.¹⁰⁷⁴ A group of sodium alkyl sulfinates and sulfonates consisting of the ethyl, propyl, butyl and pentyl derivatives has been studied by Houlton and Tartar.⁷⁵⁴ Milone contends that the dialkyl sulfates have lines at $\Delta\bar{\nu}$ 1270 and 1360 which do not appear in sulfuric acid, while the shift at $\Delta\bar{\nu}$ 980 in the sulfates is absent. Médard believes that a line near $\Delta\bar{\nu}$ 400 is characteristic of molecules containing the O=S=O group. It is quite true that one would be inclined to expect a strong Raman shift near $\Delta\bar{\nu}$ 980 which apparently is absent and is replaced by a weak frequency near $\Delta\bar{\nu}$ 1000. Neither this effect nor the appearance of the shift at $\Delta\bar{\nu}$ 400 gives conclusive evidence of any double bond formation. It will be indicated in the discussion of sulfuric acid in Part III that the frequency occurring near $\Delta\bar{\nu}$ 400 is the ν_2 deformation type of vibration in a tetrahedral molecule.

Houlton and Tartar conclude that the sulfonates and sulfinates have the following structures:



and that the shifts between $\Delta\tilde{\nu}$ 1030 and 1050, as well as 1140 to 1180 are characteristic of the S—O bond. Other possible structure assignments would involve an S—Na linkage for which there is no evidence. On the other hand, the above structures contain a C—S bond. The appearance of a strong line near $\Delta\tilde{\nu}$ 663 in the sulfinates and $\Delta\tilde{\nu}$ 762 in the sulfonates is taken to indicate a carbon-to-sulfur binding. The cyclic derivatives of sulfonic acids provide, as yet, but little reliable data.

Metallo- Compounds

Metallo- derivatives of the hydrocarbons have a useful significance. If the mass of the metallic component is sufficiently great, then it is not difficult to delineate the contributions of the radical.

Some of the earliest metallo- derivatives determined were the alkylmagnesium halides, studied by Cleeton and Dufford.³⁷⁴ The ether solution of these compounds shows $\Delta\tilde{\nu}$ 1076 for methylmagnesium iodide and 1131 for methylmagnesium bromide. These do not of course represent the complete spectra. Nickel carbonyl, according to Duncan and Murray,⁴⁹⁴ yields (on a scale of 100 for intensity) $\Delta\tilde{\nu}$ 82(100), 382(20), 463(8), 601(4), 718(0), 833(2), 872(2), 913(2), 1609(2), 2043(30), 2132(5), and 2223(1). It is possible that this molecule has a structure in which all the atoms lie in a plane. The carbonyl frequencies are more in accord with those observed for C≡O than the ordinary carbonyl structure. Calculations of the Ni—C bond yield 2.4×10^5 dynes cm⁻¹ for the force constant. The phenyl metallo- derivatives have been studied by Donzelot and Chaix.⁴⁹⁸ Mercury diphenyl yields $\Delta\tilde{\nu}$ 158, 210, 651, 704, 998(8), 1024, 1574(8), 3049, and selenium diphenyl $\Delta\tilde{\nu}$ 175(5), 201(5), 249(1), 318(8), 612(5), 668(5), 999(10), 1021(8), 1067(1), 1087(8), 1157(5), 1180(1), 1325(1), 1577(7), 3054(7), 3155(1), 3207(1). The low-frequency shifts are, as to be expected, notably reinforced.

Several alkyl metallo- derivatives have been investigated by Gopala Pai.⁶³⁰ These results, together with the data on lead tetramethyl of Duncan and Murray,⁴⁹⁴ and on tetramethylsilane and tetramethylmethane by Wall and Eddy¹⁶⁵⁹ are given in Table 41. In this table, as occasionally in others, it has been necessary to correct different co-workers' estimates of intensities to a common denominator. A few weak lines estimated by Duncan and Murray as 1/100 of the intensity of lines in lead tetramethyl

Table 41.—The Raman Shifts from Hydrocarbon Metallo- Derivatives.

$C(CH_3)_4$	$Pb(CH_3)_4$	$Bi(CH_3)_3$	$Zn(CH_3)_2$	$\Delta\bar{\nu}$	$Hg(CH_3)_2$	$Hg(C_2H_5)_2$	$Sn(CH_3)_4$	$Si(CH_3)_4$
	130(8)		144(2)		156(2)	140(1)	152(7)	202
		171(4)				212(2)		
			248(1)		255(0)	259(3)	262(4)	239
						329(0)		
331	460(5)	480(8)	488(2)			486(8)		
415	473(2)		505(8)		515(8)		506(8)	
					565(1)	562(0)	526(5)	
			620(4)			633(0)		598
					700(3)			
732		784(0)						863
						958(1)	952(0)	
						1008(3)		
						1055(2)	1046(0)	
	1155(2)	1147(2)	1159(6)					
	1170(1)	1165(3)			1182(6)	1178(6)	1200(5)	
1248		1230(1)			1258(1)		1262(0)	
		1347(0)	1346(0)			1370(1)		
						1421(3)		1427
1452						1455(3)		
2893	2891(0)				2879(1)	2857(1)		
	2918(5)	2915(1)	2897(3)		2910(2)	2896(3)	2915(3)	2905
	2999(3)				2965(1)	2942(1)	2979(2)	
	3679(0)							
	3755(0)							

have been omitted or indicated by an intensity of zero. The results obtained by Gopala Pai confirmed those of Venkateswaran¹⁶¹¹ insofar as the work is duplicated. The usual C—H lines from $\Delta\bar{\nu}$ 2890 to 3000 are present, as well as lines near 1100. However, lines near $\Delta\bar{\nu}$ 1450 are absent in several of the compounds including the ethyl derivatives. For zinc dimethyl, if $\Delta\bar{\nu}$ 488 and 505 are considered a doublet, then the fundamental frequencies are $\Delta\bar{\nu}$ 144, 488 to 505, and 620. This yields a value of 1.6×10^5 dynes cm.⁻¹ for the Zn—C force constant.

If the fundamentals for mercury dimethyl are considered to be $\Delta\bar{\nu}$ 156, 515, and 700, the force constant is found to be 2.1×10^5 dynes cm.⁻¹ The spectrum of bismuth trimethyl is somewhat similar to that of arsenic trichloride, antimony trichloride, bismuth trichloride, and trimethylamine. Its fundamental frequencies are $\Delta\bar{\nu}$ 171, 460, and 1147; presumably it has a pyramid structure. The spectrum of the tetraalkyls resembles that of the tetrachlorides. The fundamental frequencies for tin tetramethyl are $\Delta\bar{\nu}$ 152, 262, 506, and for lead tetramethyl $\Delta\bar{\nu}$ 96, 165, 444, 462.

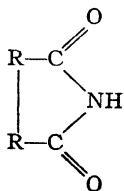
It is concluded that the dialkyl metallo- compounds may be treated as non-linear triatomic models of the type XY_2 , that the trialkyls have a pyramidal structure, and that the tetraalkyls are represented by a regular tetrahedron. There is very little doubt as to the general acceptability of this thesis. The actual assignment of specific Raman shifts to different modes of vibration could be improved if polarization measurements were made on these compounds.

Chapter 18

The Raman Spectra of Non-Heterocyclic Compounds Containing Nitrogen

Amines and Allied Compounds

The amines have the general formula RNH_2 , ketimines the formula $\text{R}_2\text{C}=\text{NH}$, amides the formula RCONH_2 , and imido- compounds the formula



All these types are represented in the Raman spectra.

There are two inorganic compounds which help define the structure of the amines. These are ammonia, NH_3 , and hydrazine, $\text{NH}_2\text{—NH}_2$. While derivatives of the hydroxylamines and hydrazines are primarily inorganic compounds, nevertheless it will be shown that the interpretation of their constitution is so intermixed with the equivalent organic derivatives, such as tetramethylammonium hydroxide and the various methylamines, that it would seem more logical to consider these compounds under organic rather than inorganic systems. Ammonia itself will be dealt with subsequently under inorganic compounds even at the expense of some repetition. One of the reasons for this consideration of other quasi-organic or inorganic compounds at this time is to establish the N—H linkage.

It has been observed that the C—H and C—S frequencies have appeared in a spectral region which is more or less unique depending on the type of compound. It is of course well recognized that any hydrogen frequency must appear, so far as its valence vibration is concerned, in the region extending from $\Delta\bar{\nu}$ 2500 to 4400 depending on whether it is an H—S vibration for the minimum, or an H—H vibration for the maximum. The C—H vibrations rarely exceed $\Delta\bar{\nu}$ 3100 and all of these are accounted for on the basis of structure; the O—H vibrations unfortunately are broad

and extend from $\Delta\bar{\nu}$ 3100 to 3600 depending on the nature of the rest of the molecule. This is doubly disadvantageous since most of the N—H vibrations fall in the same neighborhood, namely from $\Delta\bar{\nu}$ 3200 to 3400. For those compounds which may be investigated apart from aqueous solutions this naturally presents little difficulty; for those such as the ammonium ion, which exist only in solution, this adds to the difficulty of interpreting the results.

Let the N—H vibration be considered first. Ammonia (NH_3) yields 3210(3), 3310(5), 3380(3). Hydrazine ($\text{H}_2\text{N—NH}_2$)^{775, 793, 1622} yields approximately $\Delta\bar{\nu}$ 3212(2), 3272(2), and 3340(2) and phenylhydrazine $\Delta\bar{\nu}$ 3366(2). Methylhydrazine⁷⁹³ gives rise to $\Delta\bar{\nu}$ 3177(8), 3245(8), 3317(6); 1,1-dimethylhydrazine to $\Delta\bar{\nu}$ 3143 and 3336; and 1,2-dimethylhydrazine to 3170(4), 3219(5) and 3319(3); hydroxylamine^{121, 888} yields $\Delta\bar{\nu}$ 3259(5) and $\Delta\bar{\nu}$ 3306(3). Methylamine, according to Venkateswaran and Bhagavantam,¹⁶⁴⁰ yields (for N—H only) $\Delta\bar{\nu}$ 3301(2). This is a doublet $\Delta\bar{\nu}$ 3319(5), 3378(3) as observed by Kohlrusch⁸³⁴ and Dadiou and Kohlrusch.⁴¹⁵ These lines appear at 3322, 3382(2) according to Edsall,⁵¹⁸ and are a singlet $\Delta\bar{\nu}$ 3320 according to Bernstein and Martin.¹²¹ Ethylamine⁵¹⁸ yields $\Delta\bar{\nu}$ 3308(10), 3372(4), 3678(1); dimethylamine^{431, 518} $\Delta\bar{\nu}$ 3339(6). In methylamine the $\Delta\bar{\nu}$ 3319 line is the more polarized.³³⁰ It is presumable, therefore, that the simple $\text{N} \leftrightarrow \text{H}$ vibration (ν_1 or ν_r) is near $\Delta\bar{\nu}$ 3320 for the $\text{H} \diagup \text{N} \diagdown \text{H}$ group in the amines, and the ν_3 or ν_r vibration is near $\Delta\bar{\nu}$ 3380, leaving $\Delta\bar{\nu}$ 1113 as ν_2 (or δ_r).

There are, however, other contingencies. Suppose ammonia is dissolved in water. Then instead of simply NH_3 there may be produced NH_4OH . However, this is improbable as a formula. The nitrogen

forms only four covalencies, either producing $\left[\begin{array}{c} \text{H} \\ | \\ \text{H—N—H} \\ | \\ \text{H} \end{array} \right]^+$ by the gain of a

proton or producing a neutral molecule by establishing a coördinate covalence as in $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{—N—O} \\ | \\ \text{CH}_3 \end{array}$. In times past the formula for trimethylamine oxide

was written as $\text{R}_3\text{N=O}$. It will be seen shortly that the Raman spectra evidence is contrary to these classic representations.

Consideration must be given, therefore, to the effect which is produced by the conversion of the nitrogen compounds possessing NH, NH_2 , NH_3 -groups or substituted ammonia groups to those containing only $(\text{NH}_4)^+$ or substituted ammonium groups. Ammonia (NH_3) either as a gas or an aqueous solution gives rise to three or more frequencies between $\Delta\bar{\nu}$ 3222 and 3388. However, when there is definitely an ammonium ion $(\text{NH}_4)^+$

present, as in ammonium chloride, the maximum shift occurs near $\Delta\bar{\nu}$ 3140³⁶ or, possibly, $\Delta\bar{\nu}$ 3221.⁷⁹³

Dimethylamine hydrochloride⁵¹⁸ $[(\text{CH}_3)_2(\text{H})_2\text{N}]^+ [\text{Cl}]^-$ and trimethylamine hydrochloride yield only $\Delta\bar{\nu}$ 3040(4) (approximate value) which is also present in tetramethylammonium chloride.

Ananthakrishnan^{32, 35} has studied hydrazine, dihydrochloride, hydrazine hydrate and hydroxylamine compounds. He observes for crystalline hydrazine dihydrochloride in excess of $\Delta\bar{\nu}$ 2980(2) the following: $\Delta\bar{\nu}$ 3030(0), 3075(0), 3183(0,0). The same worker reports for hydroxylamine hydrochloride beginning with $\Delta\bar{\nu}$ 2927(3), 3005(4), 3045(3), 3173(2). The sulfates give fewer lines, but no lines are present in any of the crystals at $\Delta\bar{\nu}$ 3173, which indicates an ionic crystal of the type $[\text{H}_3\text{NOH}]^+ [\text{C}]^-$.

Edsall⁵¹⁸ reports $\Delta\bar{\nu}$ 3187(3) for hydrazine dihydrochloride and $\Delta\bar{\nu}$ 3219(3), 3309(3) for the monohydrochloride. According to this author the dihydrochloride should be represented by $-\text{Cl} + \text{H}_3\text{N}-\text{NH}_3^+ \text{Cl}^-$ (assuming enough HCl present to repress the ionization) and the monohydrochloride by $-\text{Cl} + \text{H}_3\text{N}-\text{NH}_2$. None of the amino acids having the group $-\text{Cl} + \text{H}_3\text{N}-\text{R}$ ⁴³¹ shows any shifts greater than $\Delta\bar{\nu}$ 3040. Kahovec and Kohlrausch⁷⁹³ obtain from hydrazine hydrate $[(\text{H}_2\text{N}\cdot\text{NH}_3)^+ (\text{OH})^- \text{ or } \text{H}_2\text{N}\cdot\text{NH}_2\cdot 2\text{H}_2\text{O}]$: $\Delta\bar{\nu}$ 3358(5) and 3452(6).

Apparently then, all these results confirm the absence of a large Raman shift in excess of $\Delta\bar{\nu}$ 3200—and usually it does not attain this value—when the ion containing the N—H group is charged positively or, in other words, when the nitrogen changes its covalency from three to four,³⁵ and when no other uncharged N—H group is present.

The unsaturated cyclic hydrocarbon derivatives of an amine have an augmented N—H shift possibly because of the adjacent C=C group. In aniline⁴³⁴ these are $\Delta\bar{\nu}$ 3360 and 3420, but the shifts return to normal in benzylamine. Xylidine and benzaniline do not show the typical N—H shift which is present in the pyrroles at $\Delta\bar{\nu}$ 3380 and 3360 in benzamide. The absence in these cases is probably experimental rather than actual.

Before leaving the consideration of N—H large frequency shifts it should be made clear that the group between $\Delta\bar{\nu}$ 3000–3400 is not unique. In all the methylated ammonium ions, but not in the amines, at least one frequency is present, namely $\Delta\bar{\nu}$ 3040±10 (depolarized). This appearance requires at least one charged ion and a methyl group attached directly to the nitrogen atom. Trimethylamine oxide hydrochloride, $[(\text{CH}_3)_3\text{NOH}]^+ [\text{Cl}]^-$ exhibits $\Delta\bar{\nu}$ 3043(10) as the maximum shift. Probably on account of the low concentration used in the presence of water no O—H shift was noted. If the hydrocarbon radical has a methylene group adjacent to the nitrogen as in the propylammonium ion the frequency is absent. It is present in $(\text{CH}_3)_4\text{N}^+$, hence it is associated with the methyl radical and

not with the N—H. The $\Delta\bar{\nu}$ 2980 ± 10 (polarized) appears in the propylammonium ion derivative as well as in hydrazine derivatives, so it may be ascribed to either C—H or N—H. This is substantiated by the fact that in addition to $\Delta\bar{\nu}$ 2927(3) for hydroxylamine hydrochloride, there appear 2763($\frac{1}{2}$) and 2630(1) and in hydrazine hydrochloride; there are also $\Delta\bar{\nu}$ 2009(1), 2544(3), 2610(2), 2660(1), 2735(3), 2805(1), 2865(2) and 2937(2). The N—H frequencies are as complicated as the C—H, and are usually still more diffuse.

Having outlined the types of N—H displacements appearing in the amines and their derivatives the next consideration is the N—O, N—N and C—N frequencies in these compounds. The N—O linkage may be estimated from hydroxylamine and its salts. Médard¹⁰⁶⁷ has observed for the low-frequency shifts in liquid hydroxylamine $\Delta\bar{\nu}$ 897(6), 921(6), 1045(0), 1108(1), 1311(0) and 1605(3). The aqueous solution, according to Bernstein and Martin,¹²¹ yields approximately the same result with the addition of $\Delta\bar{\nu}$ 1290(1).

In crystalline hydroxylamine hydrochloride there are four weak frequencies $\Delta\bar{\nu}$ 1168, 1463, 1551 and 1571, all with intensities of ($\frac{1}{2}$). There is $\Delta\bar{\nu}$ 1493(6) ascribed to N—H bending. In the sulfate, neglecting the SO_4 lines, appear $\Delta\bar{\nu}$ 1065($\frac{1}{2}$), 1498($\frac{1}{2}$), 1547(1) and 1596(1). For the N—O bond there is $\Delta\bar{\nu}$ 999(10) in the first compound and $\Delta\bar{\nu}$ 1000(6), 1012(8) in the second. This indicates some distortion by the SO_4 -group but the results are reasonably close. Nitrogen tetroxide, containing both N—O and N—N linkages, exhibits $\Delta\bar{\nu}$ 28(1), 57(1), 79(5), 283(8), 500(5), 813(6), 1337(5), 1382(5), 1724(5) which are partially reminiscent of NO_2 . It is probable, therefore, that the N—O frequency lies between $\Delta\bar{\nu}$ 900 and 1000.

The N—N frequency may be estimated from hydrazine and its salts. For hydrazine Kahovec and Kohlrausch⁷⁹³ record $\Delta\bar{\nu}$ 876(4), 1108(5) and 1620(3) for the frequencies below the N—H linear displacements. There is, of course, no evidence of an N—Cl vibration in these hydrochlorides. Consequently the lower frequency shifts are due to N—H bending or N—N. The monohydrochloride gives rise to $\Delta\bar{\nu}$ 965(4), 1109(2), 1274($\frac{1}{2}$), 1419(1), 1530($\frac{1}{2}$) and 1630(3), according to Edsall.⁵¹⁸ He also reports for this same spectral region the following shifts for hydrazine dihydrochloride: $\Delta\bar{\nu}$ 968(1), 1036(5), 1110($\frac{1}{2}$), 1645(2) (?). Ananthakrishnan³⁵ observes two frequencies, one at $\Delta\bar{\nu}$ 1519(3) and the other at $\Delta\bar{\nu}$ 1594(1) in crystalline hydroxylamine hydrochloride. These are augmented by about 20 wave numbers in the sulfate. In addition $\Delta\bar{\nu}$ 1024(10) appears which corresponds to Edsall's $\Delta\bar{\nu}$ 1036. Hydrazine hydrate,^{774, 793, 1522} both in solution and as liquid, yields approximately $\Delta\bar{\nu}$ 893(3), 1107(5) and 1617(2). It may be seen from these results that the N—N characteristic frequency may vary

appreciably depending on the type of compound, but usually appears between $\Delta\bar{\nu}$ 880 and 1050.

The N—N linkage in nitrogen tetroxide is, according to Sutherland, $\Delta\bar{\nu}$ 283, which is compatible with the characteristics of this compound—but not necessarily others—having an N—N group. The weak Raman lines mentioned above that appear between $\Delta\bar{\nu}$ 1500 and 1650 may possibly be assigned to the δ_r -type of vibration of the nonlinear $\text{H} \begin{smallmatrix} \diagup \text{N} \diagdown \\ \text{H} \end{smallmatrix}$ group.

The characteristic C—N shifts may be determined from the alkylamines. Thosar¹⁵⁶⁶ divides the lower-frequency shifts from dipropyl-di-*iso*-propylamine and dibutyl- and di-*iso*-butylamine into three groups: $\Delta\bar{\nu}$ 250-450 comprising the deformation vibration of the C—C linkage, $\Delta\bar{\nu}$ 900-1100 comprising the C—C and C—N valence vibrations, and the shifts greater than $\Delta\bar{\nu}$ 1400 which are due to the C—H linkage. The spectra of the *iso*-compounds differ in some respects from those of the normal compounds.

Table 42.—Raman Low Frequency Symmetrical Oscillations of Some of the Nitrogen Compounds.

Binding Type	Compound	Raman Shifts $\Delta\bar{\nu}$	Binding Type	Binding Shifts $\Delta\bar{\nu}$
N—O	NH ₂ OH	921(6)	N—O	921
$\overset{+}{\text{N}}$ —O	(NH ₂ OH) + Cl [−]	1000(10)	$\overset{+}{\text{N}}$ —O	1000
N—N	H ₂ N—NH ₂	880(1)	N—N	880
$\overset{+}{\text{N}}$ —N	−Cl $\overset{+}{\text{H}_2\text{N}}$ —NH ₂	965(4)	$\overset{+}{\text{N}}$ —N	965
$\overset{+}{\text{N}}$ — $\overset{+}{\text{N}}$	−Cl $\overset{+}{\text{H}_2\text{N}}$ — $\overset{+}{\text{N}}\text{H}_2$ Cl [−]	1030(5)	$\overset{+}{\text{N}}$ — $\overset{+}{\text{N}}$	1030
C—N	CH ₃ NH ₂	1040(7)		
	(CH ₃) ₂ NH	930(5)	C—N	1040
	(CH ₃) ₃ N	830(5)		
C— $\overset{+}{\text{N}}$	CH ₃ $\overset{+}{\text{N}}\text{H}_2$ Cl [−]	1000(6)	C— $\overset{+}{\text{N}}$	1000
	(CH ₃) ₂ $\overset{+}{\text{N}}\text{H}_2$ Cl [−]	895(4)		
	(CH ₃) ₂ $\overset{+}{\text{N}}\text{H}_2$ Cl [−]	821(5)		
	(CH ₃) ₃ $\overset{+}{\text{N}}$ Cl [−]	752(6)		
C— $\overset{+}{\text{N}}$ —O	(CH ₃) ₂ $\overset{+}{\text{N}}\text{OH}$ Cl [−]	754(7) 947(7)		

The lower shifts of trimethylamine³² are: $\Delta\bar{\nu}$ 275(2), 374(2)(P), 428(2), 828(6)(P), 1042(2), 1187(3)(P), 1280(0), 1404(1), 1442(3), 1472(3). If the hydrogen atoms are disregarded and the molecules treated as of the AB₃ type of symmetry C_{3v}, then below $\Delta\bar{\nu}$ 1100 there should be two polarized and two depolarized lines. The molecule, however, has five lines³²: two doubly degenerate ($\rho \approx 6/7$)(ν_4), 428(2)(D); (ν_2), 1042(2)(D), two

totally symmetrical ($\rho \ll 6/7$) (ν_3) 374(2)(P) and (ν_1) 826(6)(P), and last $\Delta\tilde{\nu}$ 275, which may be analogous to $\Delta\tilde{\nu}$ 175 in water. (Compare trimethylmethane: 370(D); 965(D), 437(P), 795(P) low frequency shifts.)

In the methylamines^{121, 518, 836} there is present a frequency near $\Delta\tilde{\nu}$ 1040(3) although in dimethylamine $\Delta\tilde{\nu}$ 930(5) appears and in trimethylamine there are $\Delta\tilde{\nu}$ 820(4) and 1030(3). In the amine hydrochlorides containing more than one methyl group, frequencies near $\Delta\tilde{\nu}$ 820, 930 and 1030 also appear but not always simultaneously. The estimated values for the C—N and N—N shifts are summarized in table 42.

These figures give an approximate value for the different types of linkage in these specific compounds. With the exception of the simplest ones it must be borne in mind that actually there is no such thing as a specific linkage determinable from this type of Raman spectra. Nevertheless, as a first approximation, it can be considered that of all the oscillations which the entire molecule undergoes, there is at least one which corresponds to what may be considered fairly close to a valence vibration. It is this specific valence vibration which is referred to above. On the simple theory, the reduction in C—N shifts as a function of increasing substitution can be accounted for by the variation in reduced mass according to the formula

$$\Delta\tilde{\nu} = 4.125\sqrt{\frac{k}{\mu}}$$

It is apparent that in most cases the charged ion has a higher frequency than the equivalent unchanged one with the possible exception of C—N and C— $\overset{+}{\text{N}}$. (The plus sign has no other significance than to indicate a charged ion or radical.)

The net result of all this is that the N—R linkages in a positively charged ion approximate 1000 and in a neutral ion $\Delta\tilde{\nu}$ 900–1050; and the N—H linkage is also affected. Frequencies in excess of $\Delta\tilde{\nu}$ 3200 are lacking in the $\overset{+}{\text{N}}$ —H compound and are present up to $\Delta\tilde{\nu}$ 3700 in some of the N—H compounds. These frequencies lead to a calculated force constant which varies from 3.6 to 4.8×10^5 dynes cm⁻¹. This excludes N₂O₄ which exhibits $\Delta\tilde{\nu}$ 283(8). Sutherland considers this as the linear N—N oscillation in this compound and this shift results in a value of 1.5×10^5 for the force constant. This substance, however, also has $\Delta\tilde{\nu}$ 813(5) which might also be considered the symmetrical vibration in the absence of polarization measurements.

From a slightly more exact treatment, from the mechanical standpoint, molecules of the type CH₃NHCH₃ can be considered as triangular. Therefore, instead of the R ↔ N oscillation of a diatomic vibrator used

thus far, these should be three frequencies: ν_1 , a symmetrical valence vibration, ν_2 a symmetrical deformation oscillation and ν_3 an asymmetrical oscillation. Of these ν_3 should be depolarized, *i. e.*, ($\rho = 6/7$) while ν_1 and ν_2 should have a value of $\rho < 6/7$. These are $\Delta\bar{\nu}$ 413(3)(P), 930(5)(P) and 1033(3)(D) which lead to a value of 4.24×10^5 dynes cm^{-1} for $\text{C} \leftrightarrow \text{N}$ motion in this compound as compared with 4.68×10^5 for the simple harmonic theory. For pyramidal molecules such as $(\text{CH}_3)_3\text{N}$ the valence force system leads to a value of 4.13×10^5 . The theory developed by Urey and Bradley¹⁶⁶¹ leads to appreciably lesser values on an absolute

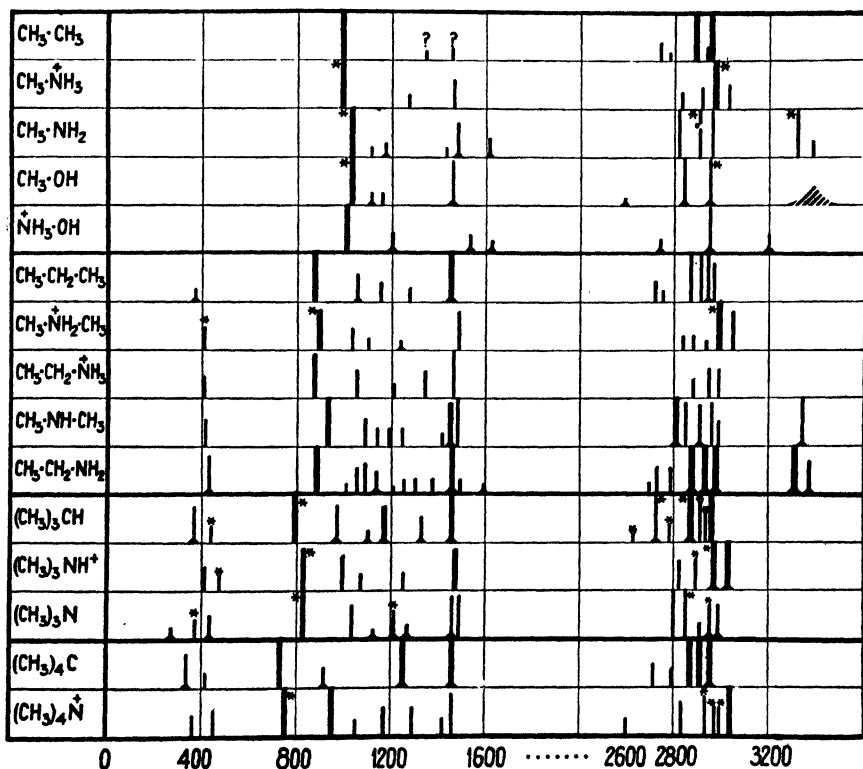


FIGURE 48. The Raman Spectra of Amines, Ammonium Ions and Related Hydrocarbons (after Edsall). The asterisks denote lines which are strongly polarized.

scale. On a comparative basis, however, approximately the same relative values of the force constant and, consequently the $\text{C} \leftrightarrow \text{N}$ vibrations, are maintained.

There is a marked similarity between the spectra of the amines and the equivalent hydrocarbon compounds. The trimethyl hydroxyl ammo-

nium ion $[(\text{CH}_3)_3\text{NOH}]^+$ bears a close resemblance for example, to the equivalent hydrocarbon alcohol *tert*-butyl alcohol. What is more surprising is the great similarity between the spectra of $[(\text{CH}_3)_4\text{N}]^+$ and $[(\text{CH}_3)_3\text{NOH}]^+$. This indicates the close equivalence of a hydroxyl group and a methyl group as components in a vibrating system. In Figure 48 are compared the spectra of some amines and hydrocarbons.

One other interesting conclusion from the work of Edsall,⁵¹⁸ Kohlrausch⁸³⁴ and Ananthakrishnan³² is the evidence against the reaction $\text{R}_3\text{N} + \text{H}_2\text{O} \rightleftharpoons \text{R}_3\text{NHOH}$. Guanidine will be discussed under the amides.

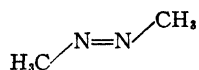
Emphasis has been placed so far on alkyl amines with occasional references to cyclic derivatives. The principal reason for this is that the determination of the normal frequency shifts of an amine is more easily accomplished by the investigation of a simple compound such as methyl amine than by the study of aniline. This is apart from the general question that there exists a possibility that the behavior of the cyclic and aliphatic compounds may be quite different due to inter- and intra-molecular compound formation. The latter has been partially discussed under the dibasic acids and the polysubstituted derivatives of benzene, and is frequently described as chelation or hydrogen bonding. The amines give little evidence concerning this problem from the point of view of Raman spectra. The discussions, so far as they are available, agree with those of Wulf and Liddel who investigated some 52 compounds containing the NH -, NH_2 - or OH -groups by means of infrared absorption. These spectra probably result solely from simple vibration absorption in various parts of the molecule and may be measurably influenced through coupling of the absorbing group with the other nearby adjacent groups in the molecule. Freymann and her co-workers^{562, 564, 565} by means of infrared absorption spectra came to the same conclusion as Hilbert, Wulf, Hendricks and Liddel that there is a modification of the normal vibrations as a result of hydrogen bonding. No static formula can correctly represent the constitution or the absence of vibrations corresponding to the NH - or OH -group. Since these interpretations are based principally upon infrared absorption, a discussion of which has been assiduously avoided except under exceptional circumstances, reference should be made to the original literature for a complete delineation of the structure of these compounds as determined by this means.

The aryl amines have been studied principally by Bonino and Brull,²¹⁴ Cabannes and Rousset,^{328, 329, 330} Dadiou and Kohlrausch,⁴¹⁵ Dadiou, Pongratz and Kohlrausch,⁴⁴⁷ Pal and Sen Gupta¹²⁰³ and others. The frequency which has been ascribed to the double bond shift occurs near $\Delta\tilde{\nu}$ 1600 and is commonly a doublet. Whether one of these shifts represents a combination frequency as occurs in benzene has not yet been conclusively

demonstrated. There is, however, in aniline a strong Raman line at $\Delta\bar{\nu}$ 815 which is polarized, the harmonic of which may interact with the frequency observed in the infrared at $\Delta\bar{\nu}$ 1640. In aniline the shift at $\Delta\bar{\nu}$ 1602 is depolarized, having a depolarization constant ρ of 0.75. The N—H shifts occur near $\Delta\bar{\nu}$ 3360 in aniline and at slightly higher values in its derivatives.

Azomethane, 1,2-Dimethylhydrazine and Acetaldazine

Although these three compounds are not directly related to the amines, from the point of view of composition they are probably as closely connected with this group as with any other. For a complete picture of the constitutional problems in connection with these compounds reference should be made to the discussion of hydrazine in this chapter and also to the treatment of azides and hydrazoic acid in Part III. Penney and Sutherland, from theoretical considerations, have come to the conclusion that the hydrazine molecule is strongly asymmetric. It is also shown that as a result of the hindrance to free rotation around the N—N bond the most stable arrangement is that in which the bonds radiate from each nitrogen atom at an angle of about 110° . This lack of free rotation is similar to that which has been proposed also for hydrogen peroxide. West and Killingsworth¹⁶⁸² have investigated azomethane and conclude that its structure is somewhat similar to that proposed for hydrazine. In the case of azomethane, however, there is the very definite alternative of *cis* and *trans* modifications, and the absence of a permanent moment is in favor of the latter. The spectral results are also in accord with the *trans* configuration:



This arrangement has a center of symmetry and will have two sets of fundamental frequencies, one of which will be active in Raman spectra only and the other in infrared absorptior only. The corresponding *cis* form has no center of symmetry and certain modes of vibration will be present in both infrared and Raman spectra.

The Raman spectrum of liquid azomethane gives rise to twelve strong Raman lines and the infrared absorption consists of ten bands, making a total of 22 out of 24 possible vibrations. However, not all of these are fundamentals. The significant factor, however, is that with one exception there are no coincidences between the Raman lines and infrared absorption. This is good evidence in favor of the C_{2h} symmetry. Apart from the vibrations in the methyl radical the Raman frequencies group themselves into three sets adjacent to the three strong lines $\Delta\bar{\nu}$ 596, 922

and 1422, which are ascribed to the totally symmetrical vibrations of the azomethane molecule. The frequencies obtained from azomethane are shown in Table 43, together with those of 1,2-dimethylhydrazine and acetaldazine.

Table 43.—The Raman Spectra of Azomethane, 1,2-Dimethylhydrazine and Acetaldazine.

Azomethane		1,2-Dimethylhydrazine		Acetaldazine	
$\Delta\bar{\nu}$	i	$\Delta\bar{\nu}$	i	$\Delta\bar{\nu}$	i
548	1	473	2	374	0
596	8	1010	2	499	5
922	4	1118	2	907	4
1023	1	1201	2	1029	3
1182	3	1301	2	1151	4
1376	5	1465	5	1345	5
1442	9	2790	6	1389	4
1576	4	2838	4	1443	5
2733	2	2867	4	1530	0
2874	2	2940	10	1569	2
2914	10	2973	9	1627	10
2985	8	3099	3	2866	2
		3226	10	2925	8
		3319	6	2959	2
		3390	2		

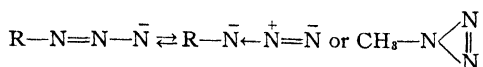
These results are in substantial agreement with those of Kahovec, Kohlrausch, Reitz and Wagner⁷⁹⁵ as far as azomethane is concerned, but differ appreciably for the dimethylhydrazine. The latter authors report a series of five weak lines between 186 and 1000, two lines at $\Delta\bar{\nu}$ 1405 and 1446, and $\Delta\bar{\nu}$ 3170 not observed by West and Killingsworth.

Referring again to the three totally symmetrical vibrations named above, the one at $\Delta\bar{\nu}$ 1442 is ascribed to the N=N and $\Delta\bar{\nu}$ 922 to C—N leaving $\Delta\bar{\nu}$ 596 as a bending type of vibration. The low value of the N=N frequency is ascribed to the fact that this bond seems reasonably to be derived from the $^3\Sigma_u^+$ state rather than the triplet $^3\pi$ state of the molecule, which leads to the conclusion that this is a double bond, in common parlance, although it is essentially weaker than the ethylenic or carbonyl double bonds. The three antisymmetrical vibrations which are infrared active are $\Delta\bar{\nu}$ 700, 730 and 1013. The molecule with the symmetry C_{2h} would have ordinarily three modes of vibrations each symmetrical with respect to the symmetry center and active in Raman scattering, together with three antisymmetrical vibrations active in infrared absorption. The coincidence of the Raman frequency near $\Delta\bar{\nu}$ 1430 with infrared absorption is considered to be accidental. Its origin is the antisymmetrical bending vibration of the hydrogen atoms in the methyl groups, while the vibration near $\Delta\bar{\nu}$ 1376 is the corresponding symmetrical vibration.

Dimethylhydrazine also shows characteristics of a strongly asymmetric

molecule. There are no strong lines except those corresponding to the C—H and N—H vibrations near $\Delta\tilde{\nu}$ 2900 and 3300. In particular there is no strong line near $\Delta\tilde{\nu}$ 1000 which would be expected if the two halves of the molecule vibrated symmetrically with respect to each other. It is assumed that the symmetry in dimethylhydrazine is essentially the same as that postulated by Penney and Sutherland in hydrazine, to which reference already has been made. In the disubstituted hydrazine there are three possible configurations of which the most asymmetrical one seems the most probable.

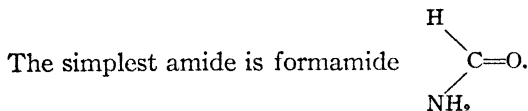
As far as acetaldazine is concerned the chief conclusions which can be drawn are that the structure is asymmetric and that the C=N vibration corresponds to $\Delta\tilde{\nu}$ 1627. The structure of methyl azide may be written as



In conjunction with this structure it should be mentioned that the azide ion is considered ^{795, 965} in the inorganic section (Part III). According to Langseth, Nielsen and Sorensen ⁹⁶⁵ and Venkateswaran ¹⁶³⁹ the azide ion is believed to have the symmetry $D_{\infty h}$ for a linear symmetrical ion with ν_1 as $\Delta\tilde{\nu}$ 1438, ν_2 as 649 and ν_3 as 2047. The addition of the methyl group, as is the case with hydrogen in hydrazoic acid, produces an unsymmetrical molecule with the methyl group at an angle of approximately 135° from the N_3 axis. The configuration involving a ring structure as well as the allenic

$\text{R}-\text{N}=\text{N}=\text{N}$ structure is held to be untenable. The Raman shifts observed by Kahovec, Kohlrausch, Reitz and Wagner ⁷⁹⁵ for methyl azide comprise some thirteen lines, the strong ones being $\Delta\tilde{\nu}$ 259(>10), 668(5), 898(>10), 1276(9), 1424(4), 1461(4), 2104(5), 2939(3). Most of these lines are polarized, particularly $\Delta\tilde{\nu}$ 898, 1276, 2104 and 2939. A group of lines represented by $\Delta\tilde{\nu}$ 1043, 1103, 1129 and 1174 are very weak and for the most part are depolarized. The polarized strong line near $\Delta\tilde{\nu}$ 2104 would seem to indicate the presence of a $\text{N}\equiv\text{N}$ linkage.

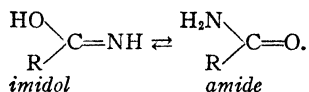
Amides



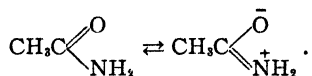
According to Thatte and Joglekar ¹⁵⁴⁸ this compound in the liquid form shows 394(1), 605(1), 726(1), 1109(1), 1306(1), 1382(2), 1675(1) and 3340(1). Acetamide possesses $\Delta\tilde{\nu}$ 377(1), 571(1), 870(3), 1400(1), 1608(1), 2940(2)

and 3375(1). The higher homologs of acetamide exhibit two carbonyl frequencies⁸⁶⁰ at $\Delta\bar{\nu}$ 1606(2) and 1664(3), although Ananthakrishnan³⁷ disagrees with this. The normal aliphatic carbonyl shift (cf. ketones) of $\Delta\bar{\nu}$ 1710 is considerably lowered by the presence of the NH_2 -group. This is reminiscent of the acids whose carbonyl shifts are at $\Delta\bar{\nu}$ 1640. It was supposed the carbonyl shifts were affected by polymerization or hydrogen bonding in the pure acids. An internal hydrogen bonding may likewise be the cause of the carbonyl frequency lowering in the amides. However, cyclic amides, such as benzamide ($\text{C}_6\text{H}_5\text{CONH}_2$), whose double-bond shifts are at $\Delta\bar{\nu}$ 1702(1) and 1651(4) and acetanilide ($\text{C}_6\text{H}_5\text{NHCOCH}_3$) which has only one such shift [$\Delta\bar{\nu}$ 1600(10)] yield conflicting results. Differentiation of the carbonyl from the ethylenic shift in the last two compounds is difficult. There is no obvious explanation from the hydrogen bond point of view, why benzamide should not be affected as much as acetamide. Last of all, the phenyl group itself tends to lower the normal carbonyl shift. In any case all the amides indicate the presence of a carbonyl frequency.

Kohlrausch and Pongratz,⁸⁶⁰ in an exhaustive study of compounds of the type $\text{X} \cdot \text{CO} \cdot \text{Y}$, indicate that the diminution of the carbonyl frequency in compounds such as $\text{H}_2\text{NCO} \cdot \text{X}$ is in the increasing order Cl, OR, H, R, SH, C_6H_5 , NH_2 . In some derivatives, such as acetamide, these authors observe $\Delta\bar{\nu}$ 1611(2), 1660(3), and in propionamide 1660(2) and 1664(4). This doubling of the frequency in this region has been considered as possibly due to a tautomeric modification of these molecules, namely



The N—H frequency in the amides is approximately the same as in the amines and is near $\Delta\bar{\nu}$ 3350. This is supported by Ananthakrishnan³⁷ from a study of crystals of acetamide and propionamide and is contradictory to the results of others.⁸⁶⁰ It is important since it tends to eliminate the possible tautomerism



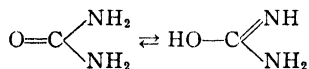
This last compound would not give rise to any frequencies in excess of $\Delta\bar{\nu}$ 3200 for reasons already given. The isoamide cannot exist exclusively because both N-methyl and N-ethyl primary amides exhibit a N—H shift at $\Delta\bar{\nu}$ 3310.

Consider next the constitution of urea on the basis of this information. Urea, H_2NCONH_2 , according to Pal and Sen Gupta¹²⁰³ manifests $\Delta\bar{\nu}$ 830, 1002, 1162, 3226 and 3374. Liquid urea according to Thatte and Joglekar¹⁵⁴⁸ gives $\Delta\bar{\nu}$ 1008(2), 1180(1), 3230(1) and 3374(1). Kohlrausch and Pongratz⁸⁶⁰ report $\Delta\bar{\nu}$ 525(2), 585(1), 1000(8), 1157(1), 1350($\frac{1}{2}$), 1458(0), 1593(2), 1655(0), 3218(1), 3383(3) and 3462(2); Ananthakrishnan³⁷ from crystalline urea, reports $\Delta\bar{\nu}$ 1012, 1171($\frac{1}{2}$), 1465($\frac{1}{2}$), 1537(2), 1576($\frac{1}{2}$), 3243(2), 3324(4), 3345(5), 3434(5); and Edsall,⁵¹⁹ 521(1), 584(1), 1000(6), 1170(1), 1468(0), 1580(0), 1666(1), 1768(?), 3230(1), 3380(3) and 3489(1).

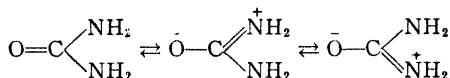
In the aqueous solution one may assume tentatively that $\Delta\bar{\nu}$ 521 and 585 exist; that $\Delta\bar{\nu}$ 1350 as well as 1768 are problematical and, finally, that $\Delta\bar{\nu}$ 1537 is possibly present. With these corrections or modifications there is good agreement between observers. This is of particular interest in the region between $\Delta\bar{\nu}$ 3200–3450. In the crystal investigations, there are no water bonds to interfere.

Ananthakrishnan attributes $\Delta\bar{\nu}$ 1537 to the bending oscillation of the N—H bond. This author believes that, if the C, N, and O atoms are regarded as being in the same plane, the molecule has the symmetry C_{2v} .

Krishnamurti, Werner and others have suggested a tautomeric arrangement



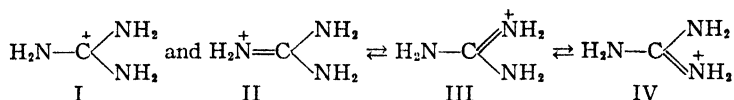
and Pauling has suggested



From the Raman spectra point of view, the problem thus presented could be easily solved if the N^+-H linkage alone were involved. In this case, as discussed under the amines, no frequency near $\Delta\bar{\nu}$ 3200 could be present for the $=\text{N}^+\text{H}_2$ linkage. But with a postulated existence of both N^+-H and $\text{N}-\text{H}_2$ the only statement that can be made is that an N—H frequency is present. Edsall,⁵²⁰ however, believes that the valence force system as applied to urea is inadequate, that the symmetry of urea is D_{2v} , and that it has a lower symmetry than exists for the guanidonium ion. The carbon-to-oxygen distance in urea is markedly lower from x-ray measurements than is the C—N distance. The molecule should give rise to six fundamental frequencies, three depolarized and three polarized according to Wilson.

None of these explanations, however, satisfactorily accounts for the existence of $\Delta\bar{\nu}$ 1537–1660 in the double-bond region.

So far as the guanidine derivatives are concerned there are four possibilities:



Pauling prefers formulas II, III or IV with a resonance of the double bond. Edsall⁵²⁰ prefers formula I on the basis of its equivalent C—N distances. This molecule should possess triagonal symmetry D_{3h} , the carbon and nitrogen atoms being coplanar. It should have three Raman frequencies ν_1 , symmetrical and polarized, two degenerate frequencies ν_2 and ν_3 ($P \approx 6/7$), and one Raman inactive frequency.

Results show 533(D), 1008(P), 1566(D), 1662(D). Therefore $\Delta\bar{\nu}$ 1008 = ν_1 ; 533 = ν_2 ; ν_3 = 1566 or 1662. Both of the latter frequencies appear⁴²⁷ in the crystalline compounds in addition to $\Delta\bar{\nu}$ 3172(1), 3238(1), 3279(1), 3338(4), 3430(1).

The calculated values of the force constant obtained on this basis are nearer to a double bond than a single bond for the C—N linkage.

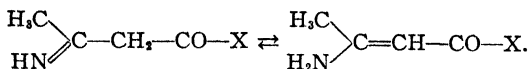
Gupta⁶⁷⁶ has also considered the guanidonium ion. This author believes

that $\text{HN}=\overset{+}{\text{C}}\begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{NH}_2 \end{array}$ is impossible from x-ray measurements, but that does not make impossible formula I or III to which reference has been made. So far as actual experimental measurements are concerned his results do not differ markedly from those already named. His conclusion agrees with the structure $\text{H}_2\text{N}-\overset{+}{\text{C}}\begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{NH}_2 \end{array}$ (I) but he believes that $\text{H}_2\text{N}-\overset{+}{\text{C}}\begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{NH}_2 \end{array}$ (IV) may exist in small proportion on account of the shift at $\Delta\bar{\nu}$ 1620. This is the nearest approximation to an amidine $\text{R}-\overset{+}{\text{C}}\begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{NH}_2 \end{array}$ which has been investigated thus far.

Imides and Imines

Of the true imides, that is, those compounds which have been derived from dibasic acids, succinimide has been found⁸⁶⁵ to give $\Delta\bar{\nu}$ 1760(4), 3332(1) for the C=O and N—H frequencies, while potassium phthalimide yields $\Delta\bar{\nu}$ 1575(2), 1599(3) and 1602($\frac{1}{2}$). Their allocation is indeterminate. So far as the N—H frequency is concerned this is obviously in the neighborhood of those compounds containing an N—H symmetrical oscillation.

Just as in the case of enol-keto tautomerism there may be an equilibrium between the ketimines and enamines according to the formula^{864, 873}



The C=N frequency is in the region of $\Delta\bar{\nu}$ 1650(3) as is indicated in Table 44. In those compounds, such as 9, 10, and 11 in the table, no isomerism

Table 44.—The C=N Frequency in Compounds of Type >C=NH .

Substance	Formula	$\Delta\bar{\nu}$
1. Amino ethylidene acetone (Ketimine form)	$\text{H}_3\text{C}-\text{CO}-\text{CH}_2-\text{C}(=\text{NH})-\text{CH}_3$	1595(2)
2. Ethyl aminocrotonate (Ketimine form)	$\text{H}_3\text{C}_2\text{O}-\text{CO}-\text{CH}_2-\text{C}(=\text{NH})-\text{CH}_3$	1615(12)
3. Urea (isoform)	$\text{H}_2\text{N}-\text{C}(=\text{NH})-\text{OH}$	1593(2)
4. Acetamide (isoform)	$\text{H}_3\text{C}-\text{C}(=\text{NH})-\text{OH}$	1611(2)
5. Propioamide (isoform)	$\text{H}_3\text{C}_2-\text{C}(=\text{NH})-\text{OH}$	1606(2)
6. Ethyl imidoacetate	$\text{H}_3\text{C}-\text{C}(=\text{NH})-\text{OC}_2\text{H}_5$	1655(5b)
7. Propyl imidoacetate	$\text{H}_3\text{C}-\text{C}(=\text{NH})-\text{OC}_3\text{H}_7$	1655(3b)
8. Ethyl imidopropionate	$\text{H}_3\text{C}_2-\text{C}(=\text{NH})-\text{OC}_2\text{H}_5$	1652(5)
9. Diethyl imidocarbonate	$\text{H}_3\text{C}_2\text{O}-\text{C}(=\text{NH})-\text{OC}_2\text{H}_5$	1658(2)
10. Methyl imidobenzoate	$\text{C}_6\text{H}_5-\text{C}(=\text{NH})-\text{OCH}_3$	1653(2)
11. Ethyl imidobenzoate	$\text{C}_6\text{H}_5-\text{C}(=\text{NH})-\text{OC}_2\text{H}_5$	1648(3)

of this type is possible, thus limiting $\Delta\bar{\nu}$ 1650 to the C=N group as in the ketimine. This also appears at the same value in dicyanodiamide.⁴³⁴ In β -dimethylaminoethylideneacetone, which normally exists in the enamine form, $\Delta\bar{\nu}$ 1548(4) and 1638(4) appear. The proper allocation of these frequencies seems to be $\Delta\bar{\nu}$ 1648 for the carbonyl and 1548 for the ethylenic linkage. Conjugation of an ethylenic group with a carbonyl group lowers the carbonyl frequency by 40 or more wave numbers. The ethylenic shift is likewise diminished by the effect of the carbonyl upon it. The amount of diminution, however, in this case is greater than can be accounted for solely by the interaction of the carbonyl group. In β -aminoethylideneacetone there appear $\Delta\bar{\nu}$ 1527(10), 1595(2) and possibly $\Delta\bar{\nu}$ 1661(0). If there were an equilibrium of the ketimine and enamine type, one would expect three frequencies in this spectral region for each of the double-bonded groups possibly present in the mixture. Off hand one would be inclined to assign $\Delta\bar{\nu}$ 1650 to the C=N grouping. However, this shift is undoubtedly lowered by the presence of a carbonyl group in the same fashion as the ethylenic shift is lowered. The effect may be not so great because the two double-bond groups, C=N and C=O, will be one carbon atom further removed from each other in the ketimine form than are the ethylenic and carbonyl groups in the enamine form. On this basis one would, therefore, assign $\Delta\bar{\nu}$ 1527 to the C=C, 1595 to C=N, and 1661 to C=O in the β -aminoethylideneacetone. This is partially substantiated by the behavior of ethyl β -aminocrotonate, which possesses $\Delta\bar{\nu}$ 1560(10), 1615(6) and 1663(3) for these three typical shifts. In ethyl

methylaminocrotonate these frequencies are $\Delta\tilde{\nu}$ 1601(8), 1648(3) and 1682(2). Where disubstitution on the nitrogen atom prevents any tautomerism only two frequencies occur.

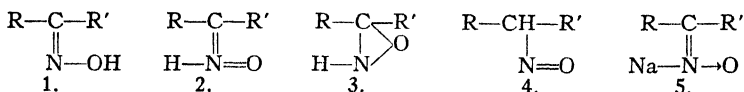
These results are of course intimately related to the possible tautomeric forms of the amides. There is no direct comparison, however, of the figures given above with those from the amides because of the lack of a simultaneous existence of two double bond groups in the molecule in the latter case. While granting that the C=N frequency normally occurs at $\Delta\tilde{\nu}$ 1650, it is a little precarious to ascribe the frequencies observed with the amides to either the *iso*- or normal form. One does not know with exactness, for example, what effect an adjacent NH₂-group would have on the carbonyl shift in an amide. Kohlrausch and Seka⁸⁷³ mentioned the existence of two double-bond shifts in urea, acetamide and propionamide, one near $\Delta\tilde{\nu}$ 1600(2) and the other at $\Delta\tilde{\nu}$ 1660(3). The lower one has been assigned to the C=N frequency in the isoamide and $\Delta\tilde{\nu}$ 1661 to the carbonyl group. This is partially supported by the disappearance of the lowest frequency on substitution of alkyl groups for the hydrogen atoms to make secondary amides.

It is to be pointed out, as Freymann and Freymann contend from infrared measurements, that in gaseous formamide neither N—H nor C=O frequencies show normal infrared absorption. Hydrogen bonding or some modification of hydrogen bonding has been suggested to explain this behavior.

The effect of a carbonyl group directly attached to a nitrogen atom which has joined to it two methyl groups such as (CH₃)₂NCOR, is to increase one of the C—H shifts in the methyl group to a value of $\Delta\tilde{\nu}$ 3023(8). This is somewhat reminiscent of the shift occurring in methylated ammonium ions at $\Delta\tilde{\nu}$ 3040. It will be remembered that this is not present in the methyl amines.

Oximes

The oximes contain the group $\begin{array}{c} \diagup \\ \text{C}=\text{NOH} \end{array}$. There are two classes, aldoximes $\begin{array}{c} \text{H} \\ \diagup \\ \text{R} \end{array} \text{C}=\text{NOH}$, and ketoximes $\begin{array}{c} \text{R}' \\ \diagup \\ \text{R} \end{array} \text{C}=\text{NOH}$, depending on whether they are derived from an aldehyde or a ketone. In addition the unsymmetrical ketoximes and aldoximes may exist in two isomeric forms. This geometric isomerism may be depicted by $\begin{array}{c} \text{R}-\text{C}-\text{R}' \\ \parallel \\ \text{N}-\text{OH} \end{array}$ $\begin{array}{c} \text{R}-\text{C}-\text{R}' \\ \parallel \\ \text{HO}-\text{N} \end{array}$. In the past there have been other representations of the possible structure of the oximes. These proposed formulas are represented as follows:



From what has been said concerning the delineation of structure from Raman spectra measurements, the spectra obtainable from the oximes would help to select the correct structure. The frequencies observed for some of the oximes studied appear in Table 45. The most salient feature

Table 45.—The Raman Shifts from Some Oximes.

Methyl ethyl ketoxime	Methyl propyl ketoxime	Methyl heptyl ketoxime	$\Delta\tilde{\nu}$ α -Benzaldoxime	Sodium benzaldoxime
351(3)			308(2)	
411(3)	377(2)	368(2)	371(2)	
525(3)	531(3)	578(2)	452(1)	473(3)
606(5)	600(3)	648(2)	511(1)	518(3)
			618(3)	
			746(1)	
802(5)	814(4)	818(4)	788(1)	
928(3)	901(1)	880(3)	858(2)	
993(4)	953(1)	947(4)	996(5)	996(4)
1082(4)	1078(2)	1003(4)	1020(2)	
		1188(4)	1180(3)	1176(3)
1261(3)		1295(5)	1207(5)	1205(4)
1426(5)	1441(5)	1430(5)	1285(2)	
			1433(2)	1440(2)
1663(5)	1658(5)	1655(5)	1603(5)	1547(5)
	2858(3)	2862(3)	1628(5)	1589(5)
2913(3)				
2948(3)	2931(3)	2928(4)		
			3052(3)	3046(3)

observable is the double-bond shift appearing near $\Delta\tilde{\nu}$ 1660(5) in the aliphatic ketoximes. It is reduced to a lower value in the aromatic aldoximes and reverts again to near $\Delta\tilde{\nu}$ 1660 in acetaldoximes. From the discussions given on the amides and imines it was indicated that a frequency in this region was consistent with the C=N linkage. This, however, does not rule out formula number 4 in view of the fact that N=O linkage also appears in this region.

Benzalaniline yields $\Delta\tilde{\nu}$ 1630 for the C=N shift which is identical with that observed from benzaldoximes. This also tends to indicate the presence of the C=N group. The C=N shift, therefore, as determined from the oximes, is indicated in Table 46. The presence of a double-bond frequency eliminates the possibility of formula No. 3. Formula No. 2 can be logically dispensed with on the ground that this type of compound would not yield a shift in the $\Delta\tilde{\nu}$ 1600 region but would substitute in its

Table 46.—Characteristic C=N Raman Shifts.

Compound	$\Delta\bar{\nu}$	
	C=N	C=C
Methyl ethyl ketoxime	1663	
Methyl propyl ketoxime	1658	
Methyl butyl ketoxime	1655	
Camphor <i>O</i> -methyloxime	1651	
α -Benzaldoxime	1628	1603
Sodium α -benzaldoxime	1547	1589
Acetophenone oxime	1623	1595
Sodium acetophenone oxime	1548	1586
Sodium <i>o</i> -chlorobenzaldoxime	1541	1583

place a strong line near $\Delta\bar{\nu}$ 1100. The coupling between two adjacent double bonds results, in the case of the allenes and ketenes, for example, in a complete change of the normal double-bond frequency. This leaves formulas Nos. 1, 4 and 5. If there is a hydroxyl group present No. 4 would be eliminated. Bernstein and Martin¹²² have observed such a frequency at $\Delta\bar{\nu}$ 3350 in acetaldoxime and at $\Delta\bar{\nu}$ 3404 in acetoxime. These authors calculated the N--O frequency in these compounds to be near 800 and the deformation oscillation to be near $\Delta\bar{\nu}$ 335. These results seem to be consistent with the structure given under No. 1. The aromatic oximes possess two double-bond frequencies, one of which is assignable to the ethylenic linkage. It is observable in the table that both the C=N and C=C frequencies are diminished in comparison with their values in the aliphatic compounds. This diminution is consistent with the diminution of the ethylenic shift as the result of conjugation, as is evidenced by the $\Delta\bar{\nu}$ 1601 frequency observed in phenylethylene. Bonino and Manzoni-Ansidei consider this diminution attributable to the perturbation caused by the establishment of the semi-polar bond such as indicated in formula No. 5. The sodium salt apparently differs quite markedly in this region of the spectrum from the normal oximes. If the sodium atom is substituted for the hydrogen in formula No. 1, its increased mass would tend to decrease the C=N frequency. Nothing is known, however, about the perturbing effect that a homopolar sodium bond would exercise on adjacent atomic vibrations. Acetaldoxime possesses a number of frequencies which are very broad and which have been attributed to two isomeric forms of this compound. The other frequencies recorded have their usual significance.

The preponderance of evidence is in favor of the generally accepted formula to depict the structure of the oximes.

Cyano- Compounds and Their Derivatives

This class of compounds is of particular interest because it illustrates the triple linkage between carbon and nitrogen. It will be recalled that the monosubstituted acetylenes gave $\Delta\bar{\nu}$ 2120 and the disubstituted acety-

lenes $\Delta\bar{\nu}$ 2235 and 2305 for the $\text{C}\equiv\text{C}$ linkage. The simplest cyanide is HCN. According to Bhagavantam¹³⁵ the shifts obtained are $\Delta\bar{\nu}$ 2076, 2097 and 2122, of which the middle shift is the strongest. Dadiou^{397, 402} obtained $\Delta\bar{\nu}$ 2094 and 2062. The 2062 shift was attributed to the isomer HNC. Other organic and inorganic nitriles have been investigated by Dadiou,^{397, 402} Dadiou and Kohlrausch,^{419, 422, 423, 424, 426, 430} Cheng,³⁶⁴ Kastler,⁸⁰³ Lechner,⁹⁶⁹ Venkateswaran,¹⁶¹⁹ Kopper and Pongratz,⁸⁹⁶ de Hemp-tinne and Wouters,⁷¹⁸ Pal and Sen Gupta,¹²⁰³ Petrikaln and Hochberg,^{1224, 1225} Badger,⁷⁷ Howlett,⁷⁶⁶ and others. Beginning with acetonitrile and ending with isocapronitrile there is complete agreement between observers that the characteristic shift of these compounds for this linkage is $\Delta\bar{\nu}$ 2245(6) as an average. This is not far removed from the frequency observed in the acetylenes for the triple-bond linkage. This is further evidence of a rough correspondence between the strength of the $\text{C}-\text{C}$ and $\text{C}\equiv\text{N}$ bonds and the observed shifts. One of the earliest demonstrations of the utility of the Raman spectra method in determining the structure of organic compounds was its application to the isonitriles. The derivatives investigated were the methyl and ethyl isonitriles. For these compounds Dadiou obtained $\Delta\bar{\nu}$ 2146(7) and 2161(5), respectively. This shows clearly that a triple bond exists between the carbon and nitrogen in the nitriles and isonitriles. In the case of the latter, however, the frequency is reduced by roughly 100 wave numbers. This is approximately the magnitude of shift alteration in going from dimethylacetylene to methylacetylene. Consequently this behavior is by no means anomalous. The only wide departures from these two characteristic shifts are in cyanogen,¹²²⁵ which yields $\Delta\bar{\nu}$ 2335, and the inorganic cyanides which yield $\Delta\bar{\nu}$ 2080, comparable with the shift observed in hydrogen cyanide. As Dadiou and Kohlrausch⁴³³ have pointed out, however, this lower shift is confined to those compounds which are dissociated readily. In the complex cyanides, such as potassium ferrocyanide and in mercury cyanide, the shift appears near $\Delta\bar{\nu}$ 2150.

Cheng³⁶⁴ has studied the chlorine derivatives of acetonitrile. In going from chloroacetonitrile to trichloroacetonitrile the frequency remains unchanged. The substitution of a phenyl group, however, will reduce the average $\Delta\bar{\nu}$ 2250 shift by 25 wave numbers, so that in benzonitrile and toluonitrile or dimethylbenzonitrile the shift remains $\Delta\bar{\nu}$ 2225. Cheng believes there is a shift characteristic of the $\text{C}-\text{CN}$ group which occurs between $\Delta\bar{\nu}$ 150 and 187 in all these compounds.

The cyanamides investigated by Kahovec and Kohlrausch⁷⁹² give the expected results. There is a shift near $\Delta\bar{\nu}$ 2200 for the $\text{C}\equiv\text{N}$ linkage and there is a strong resemblance between the spectra of the cyanamides and these of corresponding acetylenes. The triple-bond shift has a slightly

greater value in the former compounds. There are, however, two compounds of this type which show no shift near $\Delta\bar{\nu}$ 2200. These are cyanamide dihydrochloride and the isomer of dipropylcyanamide $[(C_3H_7)_2N-C\equiv N]$ the structure of which may be written as $C_3H_7N=C=N-C_3H_7$. In the latter case there is the allenic type of linkage and the consequent disappearance of the $C\equiv N$ frequency and the appearance of a new one near $\Delta\bar{\nu}$ 1100. In cyanamide itself it is believed that there is an equilibrium between the two isomers, $H_2NC\equiv N$ and $HN=C=NH$, because of the weakness of the triple-bond line and because of the presence of a strong line near $\Delta\bar{\nu}$ 1100. In this case there may be present also some of the polymer, dicyanodiamide.

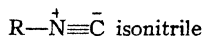
De Hemptinne and Wouters⁷¹⁸ have investigated the nitriles which contain both ethylenic and cyano- linkages in the molecule and obtained $\Delta\bar{\nu}$ 2235 and 2255 for the $C\equiv N$ groups. The ethylenic shift in vinyl nitrile is $\Delta\bar{\nu}$ 1629, in crotononitrile $\Delta\bar{\nu}$ 1645, and in isocrotononitrile $\Delta\bar{\nu}$ 1627.

Thiocyanates and Isothiocyanates

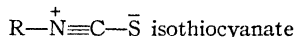
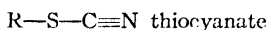
Aside from a differentiation in the structure of nitriles and isonitriles it has also been possible to investigate the thiocyanates and isothiocyanates. Dadiou, for example, observed $\Delta\bar{\nu}$ 2145(6) in methyl thiocyanate and $\Delta\bar{\nu}$ 2152(7) in ethyl thiocyanate. In ethyl isothiocyanate was observed $\Delta\bar{\nu}$ 2106(3) and 2182(2), in isobutyl isothiocyanate $\Delta\bar{\nu}$ 2100(3) and $\Delta\bar{\nu}$ 2172(3), and in phenyl isothiocyanate $\Delta\bar{\nu}$ 2100(3) and 2172(3). The constitution of the isothiocyanates was formerly indicated by $-N=C=S$. It has been suggested⁴³³ that this constitution should be $-N\equiv\overset{\text{C}}{\underset{\text{S}}{\text{I}}}$, or¹⁹⁵ $R-\overset{+}{N}\equiv C-\overset{-}{S}$. In comparing the two isomers, C_2H_5SCN and C_2H_5NCS , both show strong shifts near $\Delta\bar{\nu}$ 630 and $\Delta\bar{\nu}$ 942. There is no shift in the region corresponding to the linear vibration of the ethyl group against the SCN or NCS radical which is markedly different in the two isomers. The isothiocyanate compound shows $\Delta\bar{\nu}$ 1069(6) and 1340(3) not present in the ethyl thiocyanate. On comparing acetonitrile with methyl isonitrile, little difference appears in the spectra other than that attributable to the $C\equiv N$ linkage.

It will be recalled that the C—S shifts in the mercaptans and thioethers occurred near $\Delta\bar{\nu}$ 650 and 733. All inorganic thiocyanates exhibit a frequency at approximately $\Delta\bar{\nu}$ 745. This is reflected in both the RNCS and RSCN compounds by a strong shift varying from $\Delta\bar{\nu}$ 626 to 690.

It is apparent from the above considerations that the constitutional formula for the cyano- group in the nitriles and isonitriles may be expressed by the following:



and for the thiocyanates and isothiocyanates:



Badger ⁷⁷ has sought to explain the splitting of the $\text{N}\equiv\text{C}$ frequency in the iso- compounds, particularly the isothiocyanates, by the mechanism based on a Fermi resonance between a harmonic of $\Delta\bar{\nu}$ 1070 and 2150. This explanation should apply to the nitriles and isonitriles equally with the isothiocyanates. Unfortunately the RCN and RNC compounds, while in most cases possessing shifts near $\Delta\bar{\nu}$ 1100 and always near $\Delta\bar{\nu}$ 2150, do not exhibit the doubling of the $\text{C}\equiv\text{N}$ frequency called for by the Fermi resonance.

It is shown in the discussion of the inorganic cyanogen compounds in Part III that the $\bar{\text{S}}-\text{C}\equiv\text{N}$ ion can be treated as a molecule having the symmetry $\text{C}_{\infty v}$ where ν_1 , ν_2 and ν_3 are represented respectively by $\Delta\bar{\nu}$ 750, 400, and 2066, the ion being considered as linear. The ν_2 shift is inactive in the Raman effect but $2\nu_2$ occurs at $\Delta\bar{\nu}$ 796. Methyl thiocyanate,⁷⁹² however has three relatively strong frequencies representing chain vibrations, namely $\Delta\bar{\nu}$ 189(10), 675(7), 697(5), and the weaker vibrations at $\Delta\bar{\nu}$ 455(1), and 769(0). None of these can represent combinations. The two lines at $\Delta\bar{\nu}$ 675 and 697 apparently indicate an unobserved Raman line at $\Delta\bar{\nu}$ 345.

Isocyanates

The isocyanates have been considered to have the structure $\text{R}-\text{N}=\text{C}=\text{O}$. This structure has an air of familiarity and is more than reminiscent of the allenes ($\text{RC}=\text{C}=\text{C}-\text{R}$). The allenes show no ethylenic shift at $\Delta\bar{\nu}$ 1640 but show a strong displacement at $\Delta\bar{\nu}$ 1100. The isocyanates^{397, 896} exhibit no shift at $\Delta\bar{\nu}$ 1650 for $\text{C}=\text{N}$ or $\text{C}=\text{O}$, but have a medium strong shift at $\Delta\bar{\nu}$ 1409(5) and 1434(5) in the methyl and ethyl isocyanates respectively; $\Delta\bar{\nu}$ 1421(4) in isopropyl isocyanate, $\Delta\bar{\nu}$ 1440(5) and 1510(4) for phenylisocyanate, and $\Delta\bar{\nu}$ 1438(5) and 1513(4) for α -naphthyl isocyanate. This is excluding the $\Delta\bar{\nu}$ 1450 shifts attributable to $\text{C}-\text{H}$, which also occur in the aliphatic compounds, and the $\text{C}=\text{C}$ shift at $\Delta\bar{\nu}$ 1590, which is present in the aromatic compound. The perturbing effect of adjacent double bonds seems to reduce seriously the frequency of the $\text{C}=\text{N}$ and $\text{C}=\text{O}$ linkages. The principal point, however, is that in the isocyanates there is no characteristic $\text{C}\equiv\text{N}$ shift.

Nitrates, Nitrites, and Nitro- Compounds

The organic nitrates yield as the principal frequencies of the NO_3 -group $\Delta\bar{\nu}$ 730, 1074, 1391, and 1659. The spectrum of concentrated nitric acid

yields $\Delta\bar{\nu}$ 607, 667, 916, 1292, 1665, and 1685, which spectrum radically alters with dilution.

The organic nitrogen oxide derivatives have been investigated by Dadiou, Jele, and Kohlrausch,⁴⁰⁶ Dadiou and Kohlrausch,^{428, 432} Ganesan and Venkateswaran,⁵⁷⁷ Milone,¹⁰⁹⁷ Médard,^{1069, 1070} Médard and Alquier,¹⁰⁷² Petrikaln and Hochberg,¹²²² Ganesan and Thatte,^{575, 576} and Thatte and Ganesan.¹⁶⁴⁴ These compounds are characterized by the relative intensity of their identifying shifts. The frequencies of the NO₃, or more correctly the O—NO₂ group, are on the average $\Delta\bar{\nu}$ 575, 868, 1290, and 1640. These may vary somewhat from compound to compound but are easily recognizable from their intensities. In Table 47 are given all except the weakest

Table 47.—The Raman Shifts from Alkyl Nitrates.

$\Delta\bar{\nu}$									
CH ₃ NO ₂	C ₂ H ₅ NO ₂	C ₃ H ₇ NO ₂	C ₄ H ₉ NO ₂	C ₅ H ₁₁ NO ₂	C ₆ H ₁₃ NO ₂	C ₇ H ₁₅ NO ₂	C ₈ H ₁₇ NO ₂	C ₉ H ₁₉ NO ₂	C ₁₀ H ₂₁ NO ₂
365(5)	385(5)	352(5)							
582(7)	570(5)	571(5)	569(5)	574(5)	573(5)	570(5)	570(5)	570(5)	568(5)
		611(1)		616(5)	615(5)				
669(5)	657(1)		702(5)	706(5)					
864(7)	864(5)	866(5)	848(5)	869(7)	869(7)	864(7)	864(8)	862(8)	861(8)
			880(5)						
1290(10)	1285(7)	1282(7)	1281(7)	1285(7)	1283(1)	1284(5)	1080(5)	1080(5)	1078(5)
				1315(5)	1313(5)		1280(5)	1279(5)	1279(5)
				1392(5)		1388(5)	1307(5)	1308(5)	1307(5)
1437(5)				1450(5)	1439(8)		1440(5)	1441(5)	1440(5)
1460(5)	1455(5)	1454(5)		1473(5)	1476(8)	1455(5)	1463(5)	1464(1)	1464(1)
				1531(1)		1568(5)			
1644(8)	1633(5)	1635(5)	1632(5)	1640(8)	1640(8)	1632(5)	1635(5)	1635(5)	1633(5)
	2725(1)	2739(1)	2744(1)	2741(1)	2744(1)	2730(1)			
2839(1)	2890(1)	2888(1)	2881(1)	2881(1)	2878(1)	2852(1)	2885(5)	2885(5)	2857(5)
						2899(5)	2899(8)	2897(8)	2895(5)
2910(5)			2917(5)	2920(7)	2916(5)				
2968(7)	2948(7)	2945(7)	2941(7)	2949(7)	2943(7)	2936(7)	2936(5)	2933(5)	2936(5)
	2991(7)	2985(5)	2976(5)	2980(5)	2973(5)	2968(5)	2967(5)	2963(5)	2963(5)
3047(5)									

lines for ten organic nitrates, taken from the work of Médard¹⁰⁶⁹ and of Médard and Alquier.¹⁰⁷² It is presumed by Médard that the frequencies at $\Delta\bar{\nu}$ 1307 and 1455 pertain to the CH₂- and CH₃-groups, respectively, and those between $\Delta\bar{\nu}$ 2700 and 3047 to the C—H oscillation. Many of the frequencies observed are common to those obtained from the aliphatic alcohols and hydrocarbons. However, there are some peculiarities. The shift near $\Delta\bar{\nu}$ 1450 appears as a doublet beginning with amyl nitrate, becomes a single line in heptyl nitrate, and appears again as a doublet in the remainder of the series. The shift at $\Delta\bar{\nu}$ 1080(5) appears only in nonyl, decyl and dodecyl nitrates with any intensity. It is present, but faint, in lower homologs. The shift at $\Delta\bar{\nu}$ 1640 may be indicative of the N=O binding as the ethylenic shift is indicative of the C=C binding. Although the two lower frequencies in concentrated nitric acid are somewhat dis-

placed, there is a general correspondence between the frequencies observed in this compound and those obtained from the organic O—NO_2 -group. This is in contradistinction to the complete lack of agreement between the R—NO_2 frequencies and those observed in the alkali nitrates. Consequently there is a reasonable presumption that concentrated nitric acid has the ester structure HO—NO_2 in lieu of the structure HNO_3 . On dilution, however, the HNO_3 frequencies are so modified that there is unquestionably a conversion to the nitrate ion identical with the alkali nitrates.

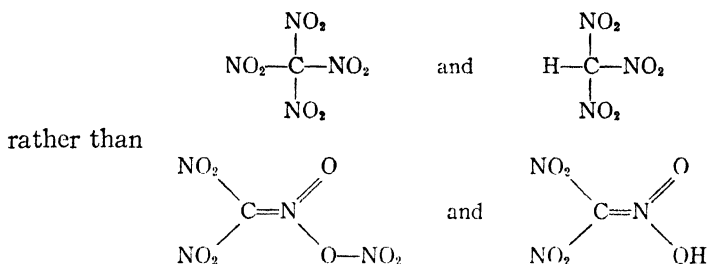
In Table 48 are given the Raman spectra of some of the substituted nitromethanes and nitrites. Apparently the characteristic frequencies of the nitro- group are approximately $\Delta\tilde{\nu}$ 420, 1340, 1607. In the higher

Table 48.—The Principal Raman Shifts of Some Aliphatic Nitrites and Nitro- Compounds.

CH_3NO_2	$\text{CH}(\text{NO}_2)_2$	$\text{C}(\text{NO}_2)_4$	$\text{C}_2\text{H}_5\text{NO}_2$	$\text{C}_6\text{H}_{11}\text{NO}_2$	CH_3ONO	$\text{C}_4\text{H}_9\text{ONO}$
		193(5)				
	200(5)	227(5)	295(3)	255(2)		
	374(7)	355(10)	389(2)	349(1)	364(2)	
483(5)	410(8)	410(5)	492(5)			
					580(4)	
657(8)			614(4)	603(2)	610(2)	605(3)
				769(3)		796(2)
	837(5)	857(7)	875(8)		833(3)	833(3)
918(10)	942(8)	998(5)	995(3)	904(5)		
			1101(4)	1128(3)		1123(2)
	1249 } (8)	1270(7)				
	1307 }					
	1309 }					
	1366 } (10)	1342(5)	1367(7)	1342(2)		
1376(7)	1371(7)		1394(5)	1379(5)		
1402(7)			1447(4)	1455(4)	1431(2)	1438(6)
1560(5)			1556(4)	1551(3)		
	1613(7)	1610(8)			1603(3)	
		1646(8)			1648(8)	1640(5)
				2873(3)		
2968(7)			2950(7)	2965(4)		2915(5)
			2998(3)			2937(3)
3057(1)						

homologs of the nitrites the doublet appearing between $\Delta\tilde{\nu}$ 1600 to 1650 in methyl nitrite reduces to a single frequency at $\Delta\tilde{\nu}$ 1640. Consequently the nitrates and nitrites have the common frequency $\Delta\tilde{\nu}$ 1640, which is displaced at $\Delta\tilde{\nu}$ 1590 in the nitro- compounds. The nitro- group possesses $\Delta\tilde{\nu}$ 1376, which is 1290 in the nitrates and non-existent in the nitrites. By these strong lines alone these compounds can be easily identified. Pendl, Reitz and Sabathy (Raman Jubilee volume) postulate that $\Delta\tilde{\nu}$ 1330–40 for the nitro- compounds may be the result of Fermi resonance. The shift near $\Delta\tilde{\nu}$ 1370 is moderately polarized and could be considered the sym-

metrical valence vibration of the nitro- group because the other shifts between $\Delta\bar{\nu}$ 1550 and 1650 are completely depolarized. The other Raman lines that are polarized in nitromethane are $\Delta\bar{\nu}$ 915 and 2965 corresponding to the C—N and C—H valence vibrations. The inorganic nitrites possess $\Delta\bar{\nu}$ 696, 785, 1303 to 1330. No $\Delta\bar{\nu}$ 1600 was observed. It is to be remarked that the inorganic nitrites have been little investigated, and there is little correlation between these organic and inorganic observations. This would possibly indicate a true NO₂-group in this case rather than an O—N=O group. Médard considers the C—N linkage as varying from $\Delta\bar{\nu}$ 910 to 850 in the nitro- compounds. It is believed by Médard that the structures of the nitromethanes are



Chloropicrin and bromopicrin, observed by Milone,¹⁰⁹⁷ yield among other lines $\Delta\bar{\nu}$ 420, 1333, and 1578 as constant frequencies. It is possible that the $\Delta\bar{\nu}$ 1575 to 1650 frequency is attributable to the C=N linkage rather than to the N=O. This has been discussed under the oximes. In N₂O the shifts are $\Delta\bar{\nu}$ 1284 and 2224, indicating a triple bond (N≡N) group and possibly an N=O group, although the N=O shift in NO is $\Delta\bar{\nu}$ 1877. The inorganic nitrites and nitrates are considered in detail in Part III.

The cyclic nitro- derivatives yield a strong line $\Delta\bar{\nu}$ 1340, $\Delta\bar{\nu}$ 1520 to 1590.

Chapter 19

The Raman Spectra of Some Heterocyclic Compounds

Furans

The first of the heterocyclic systems to be considered will be the five-membered rings with oxygen as the hetero-atom. In this series furan has been the most investigated. This has been studied by Bonino,^{203, 204} Bonino and Manzoni-Ansidei,²³¹ Catlin and Wilhelm,³⁵⁰ Glockler and Wiener,⁶¹⁶ Médard,¹⁰⁶⁵ Prévost, Donzelot, and Bolla,¹²⁵⁵ and Reitz.¹³⁶² It will be remembered that cyclopentadiene gave $\Delta\tilde{\nu}$ 1500(5) in contrast to $\Delta\tilde{\nu}$ 1615(7) for cyclopentene. Since furan is structurally somewhat similar to cyclopentadiene, it is to be expected that any ethylenic shift in this compound would be especially low and this is the case. The observed ethylenic shift is of the order of $\Delta\tilde{\nu}$ 1486, as obtained by Glockler and Wiener.⁶¹⁶ This was attributed by them to the furan ring. The C—H shift in furan and its derivatives occurs at approximately $\Delta\tilde{\nu}$ 3155, so far as the ring hydrogen is concerned. This is considerably in excess of the same type of shift observed in other cyclic compounds containing only carbon in the ring, although there are instances where an occasional very weak shift may equal or exceed this amount. This shift also appears in other heterocyclic five-atom rings including thiophene, although it may be somewhat displaced. The derivatives of furan have been studied by Bonino and Manzoni-Ansidei,²³¹ Glockler and Wiener,⁶¹⁶ and Matsuno and Han.^{1043, 1046} The results are indicated in Table 49 for furan and three typical derivatives. The data on the derivatives given in this table are taken principally from the work of two of the above-named authors,^{616, 1043} while the data on furan are largely from the complete work on this compound which has been carried out by Reitz.¹³⁶¹

There is one point which stands out strikingly in these results, namely, that on the introduction of a side-chain the ethylenic shift is augmented at times by as much as 150 wave numbers, although it is not too certain to what mode of oscillation this shift may be assigned. In 2-methylfuran, for example, instead of $\Delta\tilde{\nu}$ 1486 observed in furan, the double-bond frequency becomes either $\Delta\tilde{\nu}$ 1510 or 1605. The augmentation is independent of the constitution of the side-chain, which may contain an alcohol, aldehyde or ester group. In practically all cases doublet shifts appear, con-

Table 49.—The Raman Shifts from Furan and Its Derivatives.

Furan*			$\Delta\tilde{\nu}$ 2-Methylfuran	2-Furaldehyde	Methyl α -furoate
				172(4)	170(2)
			253(5)	218(1)	233(5)
			343(3)		395(4)
483	(0)			497(3)	443(3)
				581(1)	
604	(0)	(0.86)	626(3)	624(1)	602(1)
			654(6)		618(2)
735	(0)	(0.63)	718(1)	758(1)	770(3)
839		D	796(1)		798(6)
857	(0)		883(3)	878(3)	888(6)
874	(1)	(0.84)	917(4)	929(5)	911(5)
990	(1)	(0.27)			922(8)
1039	(1)	D	1018(3)	1021(3)	1019(6)
1058	(3)	(0.22)	1084(8)	1078(3)	1081(6)
1139	(10)	(0.15)	1147(3)	1156(6)	1122(5)
1169	(0)	D	1215(4)	1212(1)	1172(4)
1279	(0)	D	1233(3)		1236(5)
1357	(0)		1376(3)	1378(6)	1307(4)
1381	(5)	(0.42)	1386(9)		1390(8)
1486	(7)	(0.12)	1453(4)	1467(10)	1478(10)
			1510(10)		
			1605(6)	1567(8)	1572(5)
				1677(10)	1583(6)
				1688(8)	
					1726(8)
			2745(2)	2840(1)	
			2883(3)		2845(1)
			2928(7)		
			2955(2)		2956(5)
3096	(1)	P	3119(6)	3129(3)	3122(4)
3126	(2)	P	3153(4)	3146(5)	3155(2)
3165	(3)	(0.19)			

*When more than one number is given in parentheses, the second number indicates degree of depolarization. This number is always a fraction.

nected with the ethylenic linkage. In addition to the ring double-bond shift ethylenic or carbonyl shifts may appear, if side-chains containing these bonds are added to the furan nucleus. In the case of the aldehyde derivatives there appear two, $\Delta\tilde{\nu}$ 1668 and 1688. Both of these frequencies were observed by Kohlrausch, Pongratz, and Seka⁸⁶⁵ and by Matsuno and Han, but not by Glockler. In the esters appear $\Delta\tilde{\nu}$ 1721 to 1745 of the carbonyl frequencies, depending on the ester group. Consequently it is to be noted that the carbonyl frequency is increased by the presence of the furan group. There is also present a shift which remains fairly constant near $\Delta\tilde{\nu}$ 1000, which might possibly be attributable to the C—O linkage. Matsuno and Han have discussed attributing the frequencies to the various derivatives. The lines corresponding to $\Delta\tilde{\nu}$ 888, 1088, and 1390 are found in most five-atom rings. They believe that $\Delta\tilde{\nu}$ 1507 and 1605 are characteristic of a furan derivative containing CH_2 in the side-chain. The α -derivatives of furan give $\Delta\tilde{\nu}$ 1460 and 1507, which are not

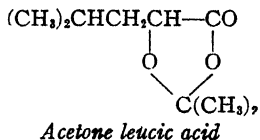
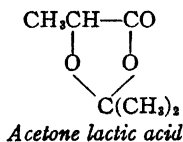
assigned to the transverse vibration of the hydrogen. These frequencies are associated with the furan ring. It is believed that the double-bond formula for these compounds is more probable than the centric formula.

According to Médard¹⁰⁶⁵ the frequencies characteristic of the furan ring are $\Delta\tilde{\nu}$ 610, 745, 880, 1150, 1390 and 1500. These are not found in tetrahydromethylfuran. The change in the ring frequencies on substitution of a side-chain is undoubtedly related to a change in symmetry, the unsubstituted compound being the more symmetrical. Catlin and Wilhelm contend they have observed an extremely weak band of $\Delta\tilde{\nu}$ 1559 in furan. If this line is present its extreme weakness would indicate the correctness of the contention made in regard to the anomalous behavior of the ethylenic linkage. Bonino and his co-workers have postulated an equilibrium of electronic formulas to account for this behavior. This is similar in effect to the resonance type of structure proposed by Pauling. There is no doubt about the great similarity between the spectra of thiophene, furan, pyrrole, and to a certain extent cyclopentadiene. There is an especially strong resemblance between the spectra of pyrrole and furan. The substitution of an N—H group for an oxygen atom does not appreciably modify the symmetry of the molecule. If sulfur is substituted the increased mass of the sulfur atom causes more change than in the other two cases mentioned.

The polarization measurements on thiophene, furan and pyrrole are all in accord with the conception that the shifts of $\Delta\tilde{\nu}$ 1385(8) (0.13); 1486(7) (0.12); and 1465(5) (0.22) respectively, in these compounds owe their origin to the symmetrical C=C vibration. If there is any remaining doubt this may be resolved in the future by means of the spectra of the deuterium derivatives of these compounds.

Other Oxygen Rings

There are other types of heterocyclic compounds involving oxygen which are somewhat analogous to an anhydride. It has been pointed out that the anhydrides yield shifts between $\Delta\tilde{\nu}$ 1775 and 1845. The anhydrides are generally ring compounds bound together through an oxygen. The shift referred to is the carbonyl shift of the oxygen, which does not enter into the ring structure. Oeda¹¹⁸⁷ has investigated acetone lactic acid and acetone leucic acid having the formulas:



These yield $\Delta\bar{\nu}$ 1790(5) and 1787(5) for the lactic and leucic acid derivatives, respectively. These two compounds, therefore, behave like any other anhydride, but were included among the heterocyclic compounds because of their peculiar cyclic structure. Although these are five-membered rings they show no shift in excess of $\Delta\bar{\nu}$ 1450 which can be attributed to the transverse hydrogen vibration. The maximum C—H line is $\Delta\bar{\nu}$ 2994, so that the ring hydrogen does not differ materially from that observed in cyclopentane.

Dioxane, investigated by Villars,¹⁶⁴⁵ Wolkenstein and Syrkin,¹⁶⁹⁵ Williamson,¹⁶⁸⁹ Venkateswaran,¹⁶²⁵ and Kahovec and Kohlrausch⁷⁹¹ exhibits no peculiarities, the principal frequencies being the usual C—H ones and a relatively strong shift in $\Delta\bar{\nu}$ 837(4). This compound gives rise to Raman lines which are somewhat related to those observed in cyclohexane. All the most important lines of cyclohexane appear more or less in the same position in dioxane. There is one outstanding difference in the intense line at $\Delta\bar{\nu}$ 1306 which appears only in dioxane. The line at $\Delta\bar{\nu}$ 425 in cyclohexane is resolved into three lines in dioxane. The comparison between the spectra obtained from dioxane and some other similarly constituted compounds such as piperidine, thioxane, dithiane, etc. is shown later in the discussion of other heterocyclic six-membered rings.

Pyrroles

The pyrroles have been studied extensively by Bonino,^{211, 208} Bonino and Manzoni-Ansidei,^{229, 232, 233, 236, 241, 242, 243, 244, 245} Bonino, Manzoni-Ansidei and Pratesi,^{253, 254} Bonino, Manzoni-Ansidei and Dinelli,²⁵⁰ Manzoni-Ansidei,¹⁰²⁷ Manzoni-Ansidei and Cavallaro,¹⁰²⁹ Redlich and Stricks,^{1357, 1360} Reitz^{1362, 1365} and Stern and Thalmayer.¹⁵⁰⁵ The pyrroles, like the furans, are five-atom rings containing one hetero-atom. The spectra which they exhibit have many similarities. As in the case of furan, pyrrole has an exceedingly low ethylenic shift. The only frequency displacements between $\Delta\bar{\nu}$ 1140 and 3073 occur at the $\Delta\bar{\nu}$ 1380 and 1465 shifts, which appear in slightly modified form in every derivative of the pyrroles and the furans. While this may be connected indirectly with the C—N linkage as shown by $\Delta\bar{\nu}$ 1367 in the nitro-compounds, this explanation is doubtful. The strongest shift occurring in pyrrole is at $\Delta\bar{\nu}$ 1140. This does not appear in its derivatives, with the possible exception of 1-acetylpyrrole. This apparently would indicate a structure reminiscent of the allenes, where the double bonds are attached to the same carbon atom. On substitution, however, the double-bond linkage appears at $\Delta\bar{\nu}$ 1571 and 1605 or $\Delta\bar{\nu}$ 1469 and 1514. This doubling of the double-bond linkage shift, if this indeed can be attributed to that, depends upon whether the substitution is in the ring or on the nitrogen atom. When the substitution

takes place on the nitrogen atom the spectrum is simpler, indicating in this case a higher degree of symmetry. These results, summarized in Table 50, are based chiefly on the observations of Bonino, Manzoni-Ansidei and Pratesi,²⁶⁴ and of Reitz.¹³⁶² The carbonyl shifts observed in the carbonyl derivatives of pyrrole are slightly elevated from the normal position. The

Table 50.—The Raman Shifts of Some Pyrroles.

Pyrrole*			$\Delta\bar{\nu}$							
			2-Methyl- pyrrole	2,5-Di- methyl- pyrrole	1-Methyl- pyrrole	1-Phenyl- pyrrole	1-Acetyl- pyrrole	2-Acetyl- pyrrole	2-Pyrrole- aldehyde	Tetra- chloro- pyrrole
556 574	(0) (0)	D	257(4)	266(4) 297(3) 393(1) 485(1)		283(3) 286(2) 409(1) 442(1)				
			338(2)		354(1)		405(1)			
									393(2)	
641	(2)	(0.9)	596(4)	603(2) 623(1) 649(1) 690(3)	607(1)	619(2)				
706	(1½)	(0.9)	648(6)	660(4) 688(2)		690(3)	644(1)			
828 852	(1) (1)	(0.9) (0.9)	710(1) 782(2)	765(1)		758(2)			691(1)	
					813(2) 868(2)					
			881(4) 953(3) 973(2)				859(2) 914(2) 967(0)	929(4)	869(2)	
1001	(1)	0.10		991(5)	962(2)	916(2) 962(2) 1001(5) 1022(1) 1047(3)			954(3)	
1035 1078	(½) (½)	D P		1034(5)	1054(4) 1084(4)		1027(0)	1045(3)		
			1089(6)				1082(0)		1087(4)	
1140 1204	(8) (0)	(0.2) (0.2)				1122(2) 1141(1) 1158(3) 1175(3) 1197(0) 1254(3) 1297(1) 1333(8)	1132(4)		1141(1)	
				1187(1) 1258(5)						
1235	(0)	(0.3)	1230(5)		1283(6)	1395(4) 1421(3)			1251(1)	
1380	(4)	(0.4)	1381(1½) 1435(4)	1367(3)	1380(7) 1415(2)		1382(3)	1367(3) 1406(4)	1315(0) 1350(5) 1400(3)	
1465	(5)	(0.22)	1469(5)	1458(3) 1514(8)	1504(3)	1501(2) 1522(4)	1468(3)		1472(4)	
			1571(1½)	1605(1)		1620(0)	1602(8)			
2786	(0)				2819(1)		1711(4)	1636(5)	1645(5) 1718(0)	
			2865(3)				2915(2)			
2917	(0)	P	2918(4)	2902(3) 2927(3) 2977(1)	2942(2)			2967(2)	2991(0)	
3062 3107 3123 3380	(1) (3) (3) (2)	(0.9) (0.4)		3107(2)	3103(2) 3130(3)	3073(1) 3117(2) 3147(2)	3135(3)		3126(1)	
			3120(4) 3378(3)	3379(1)						

*When more than one number is given in parentheses the second number indicates degree of depolarization. This number is always a fraction.

shift at $\Delta\bar{\nu}$ 3380 is consistent with the H—N linkage. Its absence in 2-acetylpyrrole and 2-pyrrolealdehyde is not entirely clear, although there may be some coupling with the carbonyl group. Bonino and his co-workers assume that $\Delta\bar{\nu}$ 1550 is associated with a central vibration somewhat analogous to that connected with the centric formula.

Notwithstanding the galaxy of publications so far enumerated on the subject of pyrrole and its derivatives, the complete interpretation of their

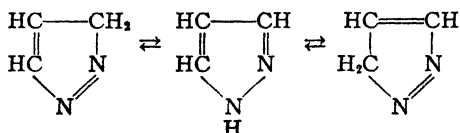
structure is not achieved. Some of the results seem to depend on the source of pyrrole²⁴³ which points to the presence of impurities. On the whole, however, the polarization measurements,¹³⁶² as has been mentioned in discussing the furans, are consistent with the view that the C=C frequency varies between $\Delta\bar{\nu}$ 1470 and 1528 depending on the nature of the substituent groups. The symmetry of the molecule is considered to be C_{2v} .²¹¹ Stern and Thalmayer¹⁵⁰⁵ attest that the presence of both C=C and C=N groups and a methylene group in pure pyrrole indicates the possible existence of a pyrollinene form. Not necessarily with reference to the pyrroles, but in general it is evident that occasionally too much credence is placed in the Biblical specification of purity.

Deuterium derivatives^{242, 244, 1360} of pyrrole are unfortunately confined solely to substitution on the nitrogen atom. These show the expected alteration of the N—H vibration from $\Delta\bar{\nu}$ 3380 to 2536. Other changes are the appearance of weak lines in the deuterium derivative at $\Delta\bar{\nu}$ 1104(0), 1012(1), 912(2), 608(2) and 456(0). The shift at $\Delta\bar{\nu}$ 1142 in pyrrole is changed to 1136 in 1-pyrrole-d. No other appreciable modification takes place in any other line.

Pyrazoles

Only a few pyrazoles^{229, 237} have been examined, such as 1-phenyl pyrazole, 1,3,5-trimethyl pyrazole,^{229, 233} the 3,5-dimethyl and 1,3,4,5-tetramethyl derivatives,²³³ and pyrazole itself. The last-named compound is more susceptible to a critical examination than the former ones. The principal point of interest is the partial lack of similarity of its spectrum with pyrrole, although there are two important lines, $\Delta\bar{\nu}$ 1149(6), and a doublet at $\Delta\bar{\nu}$ 1354(3) and 1395(2) which roughly correspond to $\Delta\bar{\nu}$ 1140 and 1380 in pyrrole, as well as a few weak ones.

However, no shift is recorded at $\Delta\bar{\nu}$ 1465 and only two shifts involving hydrogen, $\Delta\bar{\nu}$ 3062 and 3149. *These results are much more comparable to those obtained from thiophene than from pyrrole.* In particular there is no N—H shift characterized by a $\Delta\bar{\nu} > 3300$, but rather those corresponding to =C—H or pyrrole derivatives in the α -position. These observations would seem to favor a tautomerism²³⁷ of the type



Naturally, all these conclusions are based on physical measurement and the rather hopeful presumption that the purity of the original material will justify them.

In many cases the determination of characteristic Raman lines in organic compounds is difficult, particularly those pertaining to the compound as a whole. With these five-membered heterocyclic rings, however, the difficulty seems to be not to determine characteristic Raman lines, which are strong and moderately easy to secure, but to interpret them after they are obtained. It is quite evident that these compounds are very different in their constitutional structure from the six-membered rings.

Furazans, Oxdiazoles, and Azoximes

These compounds are heterocyclic five-membered rings, and are somewhat related to the furans and pyrroles. They have been investigated by Milone¹⁰⁹⁸ and Milone and Muller.¹¹⁰⁷ All these compounds contain C=N linkages, and exhibit the same peculiarities that are observed with the other cyclic compounds of this type.

The C=N shift in 3,4-dimethylfurazan presumably occurs at $\Delta\bar{\nu}$ 1461(3). This does not entirely eliminate $\Delta\bar{\nu}$ 1396(3). It may be argued that the former of these shifts is attributable to the methyl group. However, in 3,4-diphenylfurazan $\Delta\bar{\nu}$ 1448 and 1489 also appear. Furazan itself unfortunately has not been studied. The compound 3-methyl-4-phenylfurazan exhibits a number of frequencies in the region which could be assigned to double-bond frequencies. Of these, $\Delta\bar{\nu}$ 1598 is attributable to the C=C as in the benzene ring. In all the compounds involving a link between the nitrogen and oxygen atoms there is a shift near $\Delta\bar{\nu}$ 1300 to 1320, which occurs strongly in the ester form of the nitrates but not in the nitrites. A shift near $\Delta\bar{\nu}$ 2930 appears in all the compounds.

Most remarkable is the hydrogen shift occurring at $\Delta\bar{\nu}$ 3217 or higher. This is nearly in the region of the N—H characteristic linkage and may indicate some kind of tautomerism. This is further indicated by the presence of $\Delta\bar{\nu}$ 3075, which is characteristic of a hydrogen attached to C=C, and is present even in the furazan and oxdiazole derivatives, which do not contain a phenyl group.

The aliphatic oxdiazoles are particularly characterized by the shift of $\Delta\bar{\nu}$ 1579, in contrast to the much lower frequency observed with the aliphatic furazans. The aromatic substituted oxdiazoles, furazans, and azoximes exhibit a very similar group of lines falling between $\Delta\bar{\nu}$ 1440 and 1600. The oxdiazoles are characterized by the absence of a line near $\Delta\bar{\nu}$ 1300, as has been mentioned. All these results are indicated in Table 51. It is particularly interesting to note the quite different spectra of the two isomeric azoximes.

It may be generally concluded that the C=N characteristic frequency in the noncyclic compounds is near $\Delta\bar{\nu}$ 1640 to 1655, but in the multiple-bond system of the allenic type this may be reduced by more than 150 wave

Table 51.—The Raman Shifts from Furazans, Oxdiazoles and Azoximes.

3,4-Dimethyl- furazan	2,5-Dimethyl- oxdiazole	3-Methyl-4- phenylfurazan	$\Delta\bar{\nu}$ 2-Methyl-5- phenyloxidiazole	5-Methyl-3- phenylazoxime	3-Methyl-5- phenylazoxime
289(1)		283(1)			
649(1)	613(1)	621(1)	629(1)	635(1)	632(2)
709(2)					958(1)
964(1)	923(1)	998(2)	991(1)	989(2)	982(1)
	1043(1)		1030(2)	1020(1)	1036(2)
				1055(1)	1069(1)
	1108(2)		1102(2)		
		1168(2)	1175(2)		1183(2)
1308(2)		1278(1)		1305(2)	1320(1)
1396(3)					
1461(3)	1438(3)	1451(3)	1442(2)	1439(2)	1463(2)
		1502(2)	1482(3)	1483(2)	1499(2)
		1546(3)	1546(3)	1541(3)	1559(3)
	1579(3)	1598(3)	1591(2)	1576(2)	1601(2)
2938(2)	2957(2)	2936(2)	2919(2)	2928(2)	2940(1)
3070(1)	3082(1)	3083(2)	3071(2)	3065(2)	3091(2)
		3190(1)	3182(1)	3178(1)	
3217(1)					3204(1)
	3349(1)				

numbers. In the cyclic compounds the C=N frequency is considerably less than the non-cyclic compounds. If the rings are six-membered and have a multiple-bond system this shift may occur near $\Delta\bar{\nu}$ 1575. The five-membered rings exhibit a very reduced C=N shift just as the C=C shift is reduced in the C₅ cyclic or heterocyclic compounds. The double bonds in these heterocyclic compounds are very sensitive to substitution. This is not unusual, as it is to be remembered that even the transition from cyclopentene to methylcyclopentene causes an augmentation in the C=C shift of 45 wave numbers; from cyclohexene to methylcyclohexene an increase of 25 wave numbers; from cyclopentadiene to cyclopentene 115 wave numbers; and finally that in the substituted pyrroles the C=C shift appears at approximately $\Delta\bar{\nu}$ 1515 for the strongest component of a doublet, but varies considerably with substitution. The oxdiazoles, furazans and azoximes have a C=N shift, which is probably near $\Delta\bar{\nu}$ 1540 but also varies over a considerable range. The doubling of the double-bond shifts in this region for these last few compounds probably owes its origin to the lack of symmetry.

The C $\leftrightarrow$ N vibration is more difficult to estimate in cyclic compounds. It may apparently vary from $\Delta\bar{\nu}$ 930 to 1000 in the amines and isonitriles to near $\Delta\bar{\nu}$ 970 in the pyrroles, although this is also somewhat approximate. So far as the N—O is concerned the furazans, azoximes, and oximes would indicate a shift between $\Delta\bar{\nu}$ 1000 and 1078 as characteristic.

Pyridines, Quinolines and Allied Compounds

Piperidine is a saturated heterocyclic compound of the hexagonal type and consequently its Raman spectrum bears a close resemblance to that

of cyclohexane.^{791, 1112, 1455} The shifts $\Delta\bar{\nu}$ 3307 and 3339 are attributed to the well-established N—H frequency. The wing structure of $\Delta\bar{\nu}$ 1437 in cyclohexane is resolved in piperidine according to Mitra.¹¹¹² The $\Delta\bar{\nu}$ 800 frequency in cyclohexane, which is attributed to the symmetrical vibration of the carbon atoms, is displaced in piperidine to a higher frequency value, and $\Delta\bar{\nu}$ 425 in cyclohexane is split into three components. Pyridine has received considerable attention. (Note references given in compound index.) Its spectrum is similar to that of benzene. The =C—H shift occurs at $\Delta\bar{\nu}$ 3054(8) (0.4) and the C=C (or C=N) at $\Delta\bar{\nu}$ 1571(4) (6/7) or 1581, which is lower than the equivalent shift in benzene by about 15 wave numbers. The strongest frequency arising from a symmetrical ring oscillation occurs at $\Delta\bar{\nu}$ 992(10) (0.1) identical with that observed in benzene. Another strong frequency shift occurs at $\Delta\bar{\nu}$ 1029(10) (0.2).

There is no evidence of any isotope effect for the $\Delta\bar{\nu}$ 991 line as in the case of benzene. However, the resolution employed in the investigation of pyridine has been small, so that it is quite possible that this effect has been overlooked. Whiting and Martin¹⁶⁸⁴ have examined mixtures of pyridine and acetic acid and have failed to note any change in the lines of the pure substances. The abnormalities apparent in the vapor pressure and other physical properties are not visibly reflected in the Raman spectra of these compounds. Krishnamurti⁹¹⁸ on the other hand has observed appreciable changes in the position and intensities of some of the Raman lines of pyridine on dilution with water. Pyridine hydrochloride⁹¹⁸ yields $\Delta\bar{\nu}$ 3103 in place of 3054, and two new lines at 1253(1) and 1563(0). Substituted pyridines have been examined by Bonino and Manzoni-Ansidei.²²⁹ The compound 2-methylpyridine (α -picoline) differs from β -picoline in the lower frequency brackets. Both yield $\Delta\bar{\nu}$ 1373(2), 1570(2), 1599(2), and 3052.

It is quite interesting to note that compounds resembling pyridine, that is to say containing nitrogen as a part of a six-membered ring which contains only two double bonds, exhibit an ethylenic shift near its normal position. In 2,4,6-trimethyl-1,4-dihydropyridine, for example, a single frequency shift in the double-bond region is recorded at $\Delta\bar{\nu}$ 1666(2).

Quinoline yields among other shifts: $\Delta\bar{\nu}$ 1369(6), 1388(2), 1428(3), 1568(4), 1589(1), 3011(1), 3062(3); isoquinoline yields: 1379(7), 1427(2), 1458(2), 1496(1), 1554(2), 1582(2), 1622(1), 3020(3), 3058(3).

Kahovec and Kohlrausch⁷⁹¹ have compared a number of six-membered heterocyclic rings including piperazine, piperidine and cyclohexane. Cyclohexane is presumed to have the symmetry D_{3d} , pentamethylene oxide C_{2v} , dioxane C_{2h} and piperazine C_{3v} . The comparative spectra of these and other similarly constituted compounds are shown in Figure 49.

The methylindoles, peculiarly enough, exhibit no N—H shift. This is

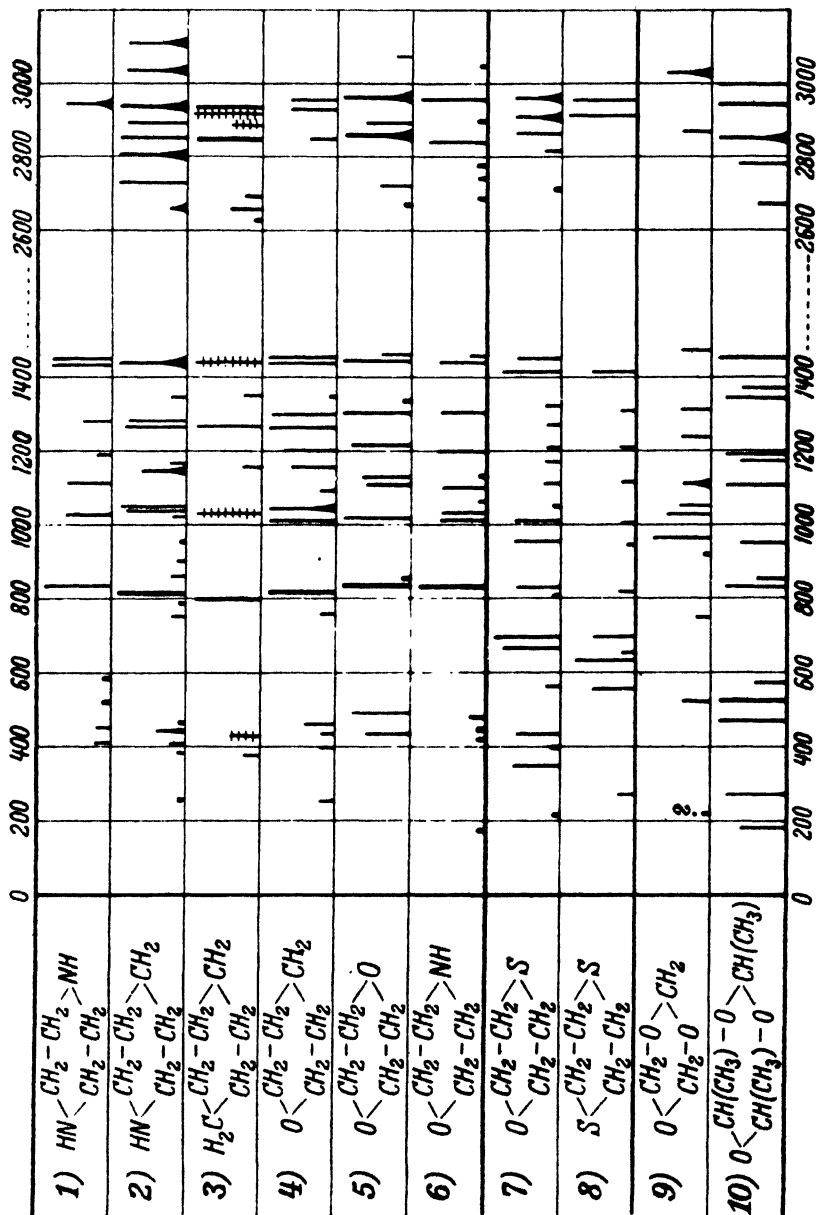


FIGURE 49. The Raman Spectra of Some Six-membered Heterocyclic Rings (after Kahovec and Kohlrausch).

probably because of a lack of recording rather than a real absence. The double-bond shifts vary considerably with the position of the substituent groups. For 2-methylindole these shifts are $\Delta\bar{\nu}$ 1554(3), 1588(2), 1615(1); for 3-methylindole $\Delta\bar{\nu}$ 1560(2), 1577(1), 1610(1); for 7-methylindole $\Delta\bar{\nu}$ 1507(2), 1600(1). Notwithstanding the careful work of Bonino and Manzoni-Ansidei on these compounds and their derivatives, no general conclusion can be drawn at this time in regard to the complete significance of these Raman frequencies. It does not seem reasonable, however, that the C=C or C=N shift can be assigned to $\Delta\bar{\nu}$ 1433 to 1480 or less in the quinoline type of compounds, as noted by Bonino and Cella,²²³ except under such conditions that no other assignment is possible.

The Raman spectra of organic compounds have been discussed from the point of view of symmetry where the data will permit a reasonable conclusion; from the standpoint of the empirical determination of characteristic frequency shifts and their use in the delineation of the structure of the compounds; and last of all from the point of view of the types of vibration of the atoms in the molecule, and the intra- and intermolecular forces. Organic compounds differ from inorganic primarily in the homogeneity of the binding forces. Ionized compounds are exceptional in organic chemistry. On the other hand inorganic substances may exist in various stages of ionization and have different degrees of binding force ranging from homopolar to completely heteropolar ones. The delineation of structure of these compounds is as important to the inorganic as to the organic fields of chemistry. Although there is not the same degree of exactness in determining inorganic structure by synthetic chemical means, and, therefore, not so sound a basis for comparison with the Raman spectra results, the inorganic compounds frequently are more simple than the organic, and hence lend themselves more readily to verification of theoretical aspects of the subject.

The same broad and general method of approach used in the discussion of organic compounds from a theoretical and empirical basis is continued in the discussion of inorganic compounds presented in Part III.

Part III

Raman Spectra of Inorganic Compounds

Organic compounds have been discussed before inorganic compounds in this book because it is generally easier to correlate structure, symmetry and interatomic forces in the former than in the latter. This is primarily because the organic chemist, by purely chemical procedure, has in most cases been able to interpret structure with a high degree of accuracy. Inorganic chemistry does not lend itself so readily to this approach. Nevertheless the theoretical basis and the conclusions which may be derived from empirical relationships are equally applicable in both cases.

Some of the simpler inorganic substances, on the other hand, have been the means by which the Raman effect has been examined from a strictly theoretical approach. The conditions under which the effect may be expected and the rules it will obey have been derived and substantiated largely by its application to inorganic chemistry. These facts, together with the utilization of empirical interpretations based on the information gained from its use in organic compounds, are applied in Part III to the elucidation of the structure and composition of inorganic substances concerning which, in too many cases, so little is really known.

Chapter 20

Raman Spectra of Gases

Hydrogen and its Isotopes

Essentially three types of Raman lines occur in gases: purely rotational Raman spectra, purely vibrational spectra, and rotational-vibrational spectra which occur when the vibrational quantum number changes and when, superimposed on this change, is a change in the rotational quantum number. The spectra of many of the compounds treated here can be obtained also in the liquid and solid states. Where such spectra are known they will be considered in this section rather than elsewhere. Those considered as gases are those that normally occur in that state. Certain gases, for example, hydrogen chloride and hydrogen bromide, are dealt with under acids since their chemical relationship to the acids is of greater interest than their relationship to other gases. All cases such as these, however, will be mentioned briefly in this section.

Of the gases, hydrogen has probably been investigated most, and recently this interest has been extended to its isotopes. The results obtained are indicated in Table 52. The figures on the deuterium compounds are taken from the work of Teal and MacWood¹⁵⁸⁶ and those on hydrogen from Rasetti.¹³²⁹ The strongest shift in hydrogen is that corresponding to $\Delta\bar{\nu}$ 4156. This is concomitant with the change in the vibrational quantum number of $0 \rightarrow 1$ and no change in ΔJ . It is the line, therefore, near $\Delta\bar{\nu}$ 4160 which corresponds to the $H \leftrightarrow H$ vibration. The shifts in hydrogen between $\Delta\bar{\nu}$ 354 and 1034 are rotational transitions occurring in the zero vibrational level; they correspond to a change in the rotational quantum number in units of two. Many of the lines occur as anti-Stokes lines. Some of these lines have been observed in liquid hydrogen by McLennan, Smith and Wilhelm.¹⁰⁵³ These correspond to $\Delta\bar{\nu}$ 356, 587 and 4156 with two anti-Stokes lines. These authors have been able to follow the conversion of *ortho* to *para* hydrogen by means of changes in the intensity of the rotational Raman spectrum as a function of time. The line corresponding to the $0 \rightarrow 2$ transition doubles in intensity in two days' time, while the $1 \rightarrow 3$ transition decreases in intensity relative to the former one. In other words, there is an increase in intensity in $\Delta\bar{\nu}$ 354 and a decrease in $\Delta\bar{\nu}$ 587.

Table 52.—The Raman Shifts from Hydrogen and its Isotopes.

	n	ΔJ	$\Delta\bar{\nu}$		n	ΔJ	$\Delta\bar{\nu}$	ρ
H_2	0—0	3 $\rightarrow$ 1	587.3	H_2	0—1	0 $\rightarrow$ 0	4162.1	0.045
		2 $\rightarrow$ 0	354.5			1 $\rightarrow$ 1	4156.0	
		0 $\rightarrow$ 2	354.1			2 $\rightarrow$ 2	4144.8	
		1 $\rightarrow$ 3	587.5			3 $\rightarrow$ 3	4126.9	
		2 $\rightarrow$ 4	814.4			0 $\rightarrow$ 2	4498.4	
		3 $\rightarrow$ 5	1034.6			1 $\rightarrow$ 3	4713.3	
HD	0—0			HD	0—1	2 $\rightarrow$ 4	4917.8	
		4 $\rightarrow$ 2	616.0			3 $\rightarrow$ 5	5109.8	
		3 $\rightarrow$ 1	443.3			2 $\rightarrow$ 0	3807.4	
		2 $\rightarrow$ 0	268.0			3 $\rightarrow$ 1	3568.9	
		0 $\rightarrow$ 2	267.1					
		1 $\rightarrow$ 3	443.0			0 $\rightarrow$ 0	3630.8	
		2 $\rightarrow$ 4	616.0			1 $\rightarrow$ 1	3628.1	
		3 $\rightarrow$ 5	784.9			2 $\rightarrow$ 2	3620.0	
D_2	0—0	4 $\rightarrow$ 6	949.3	D_2	0—1	3 $\rightarrow$ 3	3608.9	
						4 $\rightarrow$ 4	3592.5	
		6 $\rightarrow$ 4	642.2			0 $\rightarrow$ 0	—	
		5 $\rightarrow$ 3	529.2			1 $\rightarrow$ 1	2992.2	
		4 $\rightarrow$ 2	415.0			2 $\rightarrow$ 2	2986.9	
		3 $\rightarrow$ 1	297.3			3 $\rightarrow$ 3	2980.1	
		2 $\rightarrow$ 0	179.0			4 $\rightarrow$ 4	2972.4	
		0 $\rightarrow$ 2	178.8			5 $\rightarrow$ 5	2962.3	
		1 $\rightarrow$ 3	297.4			6 $\rightarrow$ 6	2948.3	
		2 $\rightarrow$ 4	414.8			0 $\rightarrow$ 2	3166.3	
		3 $\rightarrow$ 5	530.1			1 $\rightarrow$ 3	3278.5	
		4 $\rightarrow$ 6	642.3			2 $\rightarrow$ 4	3386.5	
		5 $\rightarrow$ 7	752.6					

On account of the low concentration of the scattering material the determination of the Raman spectra of gases is difficult. This has been partly solved by increasing the pressure but, as will be seen later, apart from the obvious physical limitations to such a practice, there is the additional disadvantage that the rotational transitions will not appear when the pressure exceeds the critical limits.

Hydrogen deuteride (hydrogen-d) and deuterium yield the results to be expected from a change in mass. There is a marked diminution of the frequency shifts in both of these compounds as compared to hydrogen. On the basis of a simple harmonic oscillator the calculated deuterium frequency shift would be the observed hydrogen shift divided by $\sqrt{2}$ which gives $\Delta\bar{\nu}$ 2950 compared with $\Delta\bar{\nu}$ 2992 as observed. The results of Anderson and Yost,⁵⁰ Teal and MacWood¹⁵³⁶ and Bhagavantam^{162, 163, 165} are in reasonable agreement on the spectra from these compounds where there has been a duplication of observations. Calculated and observed results are in good agreement also. Contrary to theoretical predictions, however, the 0—0 line of the Q vibrational branch of hydrogen deuteride was observed. According to Bhagavantam the phenomenon of alternating intensities is not observed and the line corresponding to the 1 $\rightarrow$ 3 transition is the most intense one in the series. In deuterium, states characterized by even rotational quantum numbers are given a statistical weight

twice as large as those having odd rotational numbers. The intensity is in quantitative agreement with the theory developed by Manneback. Polarization measurements on deuterium by Bhagavantam¹⁶⁵ indicate that the depolarization factor, ρ , is 0.18 for the vibrational Raman line. The intensity is about 1/10 of the aggregate intensity of the rotational scattering and about 1/300 of the intensity of the Rayleigh scattering.

Nitrogen

The principal transitions in nitrogen are $\Delta\bar{\nu}$ 2328 and 4633 the former corresponding to a change in the vibrational quantum number of $0 \rightarrow 1$. Some rotational scattering is observed. The results seem to support the hypothesis that in the normal state only even rotational levels are present, or at least they have a higher statistical weight than the odd ones. The spacing of the lines corresponds to $\Delta\bar{\nu}$ 16 and occurs when ΔJ equals ± 2 . Those observed are indicated in Table 53. The frequency at $\Delta\bar{\nu}$ 4633 is

Table 53.—The Raman Shifts from Nitrogen.

Vibration			Rotation	
$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	ΔJ
2328	8	0.19	60	$6 \rightleftharpoons 8$
4633	0		76	$8 \rightleftharpoons 10$
			92	$10 \rightleftharpoons 12$
			108	$12 \rightleftharpoons 14$
			124	$14 \rightleftharpoons 16$

obviously a harmonic of $\Delta\bar{\nu}$ 2328. The magnitude of the N—N vibrational shift is such as would indicate the presence of a triple bond in the chemical sense. Since Rasetti's results reported above Miller has observed some 17 Stokes and 15 anti-Stokes rotational lines including odd levels.

Table 54.—The Raman Shifts from Oxygen.

Vibration			Rotation	
$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i
1550	5	0.261	118	2.8
3085	1		106	4.3
			95	6.0
			83	7.2
			72	9.1
			60	10.0
			49	9.7
			37	8.8

Oxygen

The vibrational spectrum of oxygen¹³²⁵ is noted in Table 54. Here, as in nitrogen, there are two principal vibrational shifts, one of which is a harmonic of the other. The depolarization factor for this shift is 0.261. Some rotational scattering has been observed also, the intensities of which

are noted in Table 54. A spacing of the rotational levels corresponds to $\Delta\bar{\nu}$ 11. Taking into consideration the mass of the oxygen atoms and the force constant, the valence force will correspond to a double bond. Bhagavantam,¹³⁶ McLennan and McLeod¹⁰⁴⁹ and Sutherland¹⁵²³ have also investigated oxygen with results comparable to those so far described.

It might be mentioned that Sutherland and Gerhard¹⁵³³ observed a frequency at $\Delta\bar{\nu}$ 1280 for ozone. The weakness of the Raman spectrum is evidence against any simple symmetrical structure and suggests a non-equilateral triangle form of the molecule.

Chlorine

Although chlorine has been investigated only in the liquid form, it seems more logical to include it among the gases than among the liquids. These measurements have been carried out by Bhagavantam¹²³ and Dadiou and Kohlrausch^{432, 435} and the only Raman shift observed was $\Delta\bar{\nu}$ 556(7). Deslandres¹⁷⁹ has discussed the spectrum of chlorine from a theoretical point of view.

Carbon Dioxide

The spectrum of carbon dioxide has been determined by a number of investigators. (Refer to compound index for detailed summary of authors.) Carbon dioxide has two vibrational Raman frequencies near $\Delta\bar{\nu}$ 1284 and 1387 which appear with considerable intensity. In addition to these lines a number of rotational Raman lines are present. These results are sum-

Table 55.—The Raman Shifts from Carbon Dioxide.

Vibration			Rotation	
$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	ΔJ
1242			11.6	6 $\rightarrow$ 8
1265	1		14.8	8 $\rightarrow$ 10
1285	2	0.16-0.19	18.25	10 $\rightarrow$ 12
1305	0		21.59	12 $\rightarrow$ 14
1325	0		24.5	14 $\rightarrow$ 16
1344	0		27.6	16 $\rightarrow$ 18
1369	0		30.6	18 $\rightarrow$ 20
1383	4	0.18	34.0	20 $\rightarrow$ 22
1409	2		37.0	22 $\rightarrow$ 24
1426	0		40.2	24 $\rightarrow$ 26
1528	0		43.4	26 $\rightarrow$ 28
			46.5	28 $\rightarrow$ 30
			49.8	30 $\rightarrow$ 32
			52.5	32 $\rightarrow$ 34
			55.5	34 $\rightarrow$ 36

marized in Table 55. According to Langseth and Nielsen⁹⁶⁸ the depolarization factors for the lines $\Delta\bar{\nu}$ 1286 and 1389 are respectively 0.16 and 0.14, although Cabannes and Rousset³³¹ record a value of $\rho = 0.21$ for $\Delta\bar{\nu}$ 1389.

The intensity ratio between them indicates that the higher frequency shift is nearly twice as strong. Hanson⁶⁹² observes that, in addition to $\Delta\bar{\nu}$ 1285 and 1388, there are $\Delta\bar{\nu}$ 1244, 1409, 1426 and 1528. At higher temperatures the intensity of $\Delta\bar{\nu}$ 1409 decreases. The two frequencies $\Delta\bar{\nu}$ 1285 and 1388 are considered as two components of a doublet. Both liquid and solid carbon dioxide have been investigated by McLennan and Smith.¹⁰⁵² The frequencies at $\Delta\bar{\nu}$ 1285 and 1388 were observed in both cases. In the liquid, however, $\Delta\bar{\nu}$ 1309¹⁰⁵² and 1412¹⁴⁷ were also observed.

It has been pointed out by Langseth, Nielsen and Sørensen⁹⁶⁵ as well as by others that the perpendicular vibration in the infrared of the carbon dioxide molecule is at $\Delta\bar{\nu}$ 667. Two quanta of this vibration would correspond to $\Delta\bar{\nu}$ 1334. This is 50 wave numbers larger than the observed $\Delta\bar{\nu}$ 1285 and 50 wave numbers smaller than $\Delta\bar{\nu}$ 1384. This seems to be a case of Fermi resonance or accidental degeneracy due to the interaction of $2\nu_2$ with ν_1 . The consequence of this is the appearance of two strong Raman shifts in this region. It is well known that $\Delta\bar{\nu}$ 2350, observed in the infrared but not in the Raman effect is the parallel asymmetrical oscillation. The frequencies $\Delta\bar{\nu}$ 667 and 2359, corresponding to ν_2 and ν_3 respectively, are forbidden in the Raman effect as the molecule is both symmetrical and linear. The ν_2 deformation vibration is doubly degenerate and perpendicular.

From the spacing of the rotational frequencies, corresponding to approximately $3.2 \Delta\bar{\nu}$, observed by Houston and Lewis⁷⁵⁸ the moment of inertia $I = 70.2 \times 10^{-40}$ g.cm² is calculable. Only even rotational transitions are present.

In a chemical sense, the allenic structure $=C=$ in carbon dioxide might be expected to modify the normal carbonyl shift in the same way that the ethylenic shift is modified in ketene.

Carbon Monoxide

Carbon monoxide has only one Raman frequency, which occurs at $\Delta\bar{\nu}$ 2142 according to Amaldi.¹¹ This is in agreement with the observations of Bhagavantam,¹⁵⁷ Rasetti,^{1324, 1328, 1330} and Cabannes and Rousset³³¹ who also obtain for this shift a value of $\rho = 0.29$. The magnitude of the frequency shift for carbon monoxide is in the region which has heretofore been assigned to a triple bond from the chemical point of view. This was postulated from chemical evidence nearly thirty years ago. It is probable that this actually represents a resonant structure, the resonance occurring between double- and triple-bond forms. However, the essential behavior from the Raman spectra point of view is the same as that of any other triply bonded compound such as acetylene.

Nitric Oxide

The principal shift observed in nitric oxide by Bhagavantam¹⁵⁷ is $\Delta\bar{\nu}$ 1877 ($\rho = 0.31$).³³¹ Some unresolved rotational wings are present. Rasetti¹³³² has calculated the rotational transitions in nitric oxide.

Nitrous Oxide

Nitrous oxide, both in the gaseous and liquid forms, yields a number of frequencies. The strongest of these are $\Delta\bar{\nu}$ 1286(8) and 2224(3), according to McLennan, Smith and Wilhelm.¹⁰⁵⁵ The frequencies observed are noted in Table 56 together with the depolarization factor for the symmetrical vibration.³³¹

Table 56.—The Raman Shifts of Nitrous Oxide.

$\Delta\bar{\nu}$	ρ
1170(0)	
1185(0)	
1260(1)	
1286(8)	0.22
1315(1)	
2210(1)	
2224(3)	

According to Langseth, Nielsen and Sørensen⁹⁶⁵ the asymmetrical oscillation observable in both the infrared absorption spectrum and the Raman spectrum is $\Delta\bar{\nu}$ 2224. The symmetrical oscillation observed only in the Raman effect is $\Delta\bar{\nu}$ 1286. There is another frequency (ν_2) not seen in the Raman effect but observable in the infrared which occurs at $\Delta\bar{\nu}$ 589. A harmonic of this frequency appears at $\Delta\bar{\nu}$ 1170. Langseth and Nielsen⁹⁶⁹ have calculated the moment of inertia to be 61×10^{-40} g.cm². Not all authors have agreed on this exact value. Bender¹¹⁶ has been unable to resolve the rotational Raman spectrum of nitrous oxide.

From the observed vibrational Raman frequencies it is apparent that the molecule is linear and unsymmetrical, of symmetry $C_{\infty v}$, and that $\Delta\bar{\nu}$ 1284 corresponds to the ν_1 oscillation, $\overset{\leftarrow}{\text{N}} \overset{\leftarrow}{\text{N}} \overset{\rightarrow}{\text{O}}$, while $\Delta\bar{\nu}$ 2224 represents the ν_3 oscillation, $\overset{\rightarrow}{\text{N}} \overset{\leftarrow}{\text{N}} \overset{\rightarrow}{\text{O}}$.¹⁰⁰ The magnitude of the frequency shift would indicate the presence of a triple bond and not the structure $\text{N}=\text{N}=\text{O}$ as was formerly written. From a consideration of interatomic distances and moments of inertia of the molecule, Pauling^{1215, 1216} has recently come to the conclusion that the molecule resonates between several structures but that the effective binding over any period is $\text{N}\equiv\text{N}=\text{O}$. A similar resonance was also postulated for carbon monoxide, the triple-bonded structure predominating.

Ammonia

The Raman spectrum of ammonia has been investigated extensively. There are essentially three strong maxima in the liquid and in solution. These are, however, somewhat broad and diffuse and to some extent reminiscent of the water bands. The results are indicated in Tables 57 and 58. In gaseous ammonia the central shift, $\Delta\bar{\nu}$ 3334, is reasonably sharp.

Table 57.—The Raman Shifts of Ammonia.

Gaseous			Liquid			Solid		Solution		
$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	$\Delta\bar{\nu}$	i	ρ
934	3									
964	3		1070	0		(1070)	1?	(1073)	1?	
1922	1		1594	0		1585	0	(1615)		
(2110)	0									
(2270)	0									
3219	2		3212	4	0.20			3220	2	0.20
3334	10	0.12	3300	5	0.20	3303	1	3310	4	0.20
3520		D	3380	2	0.67	3369	4	3390	6	0.67
			3460	1				3509	0	

Rotation		
$\Delta\bar{\nu}$	i	$\Delta J = \pm 1$
79.5	2	$3 \rightleftharpoons 4$
99.5	3	$4 \rightleftharpoons 5$
119.5	2	$5 \rightleftharpoons 6$
140.0	4	$6 \rightleftharpoons 7$
158.4	2	$7 \rightleftharpoons 8$
179	4	$8 \rightleftharpoons 9$
199	1	$9 \rightleftharpoons 10$
219.5	4	$10 \rightleftharpoons 11$
236.5		$11 \rightleftharpoons 12$
257	4	$12 \rightleftharpoons 13$
295.9	3	$14 \rightleftharpoons 15$
334.5	2	$16 \rightleftharpoons 17$

Ammonia-d ₃			
	Infrared	Raman	
ν_1	2420	2420	ν_3
ν_2	2556		ν_4
			748
			1191
			786(?)
			1158

Two lower frequency oscillations at $\Delta\bar{\nu}$ 934 and 964 have been observed by Amaldi and Placzek.^{12, 13} The three frequency shifts noted between $\Delta\bar{\nu}$ 922 and 2270 are questionable. Rotational Raman spectra for ammonia gas have been observed also.⁴⁰⁵ The rotational frequencies correspond to transitions in which the rotational quantum number ΔJ changes by ± 1 as well as ± 2 and 0, which is compatible with the non-linear character of the symmetrical-top molecule. Langseth⁹⁶⁷ has analyzed the fine structure of the ammonium bands in concentrated solutions of ammonia. He observed 32 lines occurring between $\Delta\bar{\nu}$ 2962 and $\Delta\bar{\nu}$ 3661 for the rotational-vibrational transitions in which the rotational quantum number changes by ± 1 or ± 2 , corresponding to the OS and PR branches, the

Table 58.—The Raman Shifts of Aqueous Ammonia.

			Rotation		
$\Delta\bar{\nu}$	$\Delta J = \pm 1$	$\Delta = \pm 2$	$\Delta\bar{\nu}$	$\Delta J = \pm 1$	$\Delta = \pm 2$
3661	17 $\rightarrow$ 18	—	3321	—	—
3643	16 $\rightarrow$ 17	7 $\rightarrow$ 9	3311	—	—
3632	15 $\rightarrow$ 16	—	3302	—	—
3609	14 $\rightarrow$ 15	6 $\rightarrow$ 8	3290	1 $\rightarrow$ 0	—
3580	13 $\rightarrow$ 14	—	3273	2 $\rightarrow$ 1	—
3566	12 $\rightarrow$ 13	5 $\rightarrow$ 7	3254	3 $\rightarrow$ 2	2 $\rightarrow$ 0
3540	11 $\rightarrow$ 12	—	3235	4 $\rightarrow$ 3	—
3529	10 $\rightarrow$ 11	4 $\rightarrow$ 6	3226	—	—
3491	8 $\rightarrow$ 9	3 $\rightarrow$ 5	3216	5 $\rightarrow$ 4	3 $\rightarrow$ 1
3472	7 $\rightarrow$ 8	—	3178	7 $\rightarrow$ 6	4 $\rightarrow$ 2
3450	6 $\rightarrow$ 7	2 $\rightarrow$ 4	3133	9 $\rightarrow$ 8	5 $\rightarrow$ 3
3435	5 $\rightarrow$ 6	—	3099	11 $\rightarrow$ 10	6 $\rightarrow$ 4
3408	4 $\rightarrow$ 5	1 $\rightarrow$ 3	3074	12 $\rightarrow$ 11	—
3395	—	—	3050	13 $\rightarrow$ 12	7 $\rightarrow$ 5
3386	3 $\rightarrow$ 4	—	3022	15 $\rightarrow$ 14	8 $\rightarrow$ 6
3369	2 $\rightarrow$ 3	0 $\rightarrow$ 2			
3351	1 $\rightarrow$ 2	—			
3331	0 $\rightarrow$ 1	—			

Q branch being represented by the shift $\Delta\bar{\nu}$ 3312. This leads to a calculated moment of inertia 2.8×10^{-40} g.cm² for the molecule.^{957, 1688}

It was pointed out in Chapter 18 that the formation of a true ammonium ion results in a decrease in the characteristic vibrations of the N—H linkage so that the maximum frequency occurs at a value less than $\Delta\bar{\nu}$ 3250. This apparently indicates that an aqueous solution of ammonia is simply a solution of the gas in the solvent without the formation of more than a small amount of ammonium ions.^{760, 1378} The behavior of sulfur dioxide dissolved in water is similar.

Ammonia-d₃, as observed by Glockler and Wall⁶¹⁴ and Silverman and Sanderson,¹⁴³⁶ gives rise to three of the four expected vibrational frequencies. There is none too good an agreement between the observed and calculated values and between the two sets of observed values.

Howard⁷⁶⁰ has attempted to assign the frequencies observed from ammonia to different types of vibration of the pyramid. This structure, having the symmetry C_{3v} , should give rise to four Raman lines, two symmetrical and polarized and two doubly degenerate and depolarized. These frequencies are denoted by ν_1 and ν_3 representing the high and low parallel frequencies (or when the change in electric moment is parallel with the figure axis), and by ν_2 and ν_4 representing the frequencies resulting in a change of electric moment perpendicular to the axis. The latter two are the doubly degenerate oscillations. The most probable assignment of frequencies is that the $\Delta\bar{\nu}$ 950, 1631 and 3335 will correspond to ν_3 , ν_4 and ν_1 , respectively. These values are in only moderate agreement with those indicated in the tables. The ν_2 should be active in the Raman effect, but if it is present it is very weak. Two other frequencies are

present but observable only in infrared absorption. These are $\Delta\bar{\nu}$ 4417 and 5059. One of these might be accounted for as a combination between a band at $\Delta\bar{\nu}$ 3450 and 950. The $\Delta\bar{\nu}$ 3450, (ν_2) if present at all in the Raman effect, has been observed only in the liquid state. The combination of $\nu_1 + \nu_4$ might account for $\Delta\bar{\nu}$ 5057. One of the frequencies in the Raman effect at $\Delta\bar{\nu}$ 3220 quite possibly could be assigned to ν_2 . This does not appear in the infrared absorption, whereas, theoretically it should be active. Although, according to Howard, $\Delta\bar{\nu}$ 4417 might possibly be considered as the fourth fundamental, this seems to be unlikely. The bond angle calculated for ammonia chiefly from infrared data is 109° . These data lead to a calculated force constant k of 6.35×10^5 dynes cm^{-1} and a deformation force constant 0.59×10^5 dynes cm^{-1} .

It has been postulated that in the liquid form ammonia is a polymer. ^{75, 124, 427}

Carbon Oxsulfide

Carbon oxsulfide is a linear unsymmetrical molecule. The oxygen-to-carbon distance is very much less than the carbon-to-sulfur distance. Dadiou and Kohlrausch ⁴³⁷ have calculated the force constant for the C—O linkage as 13.6×10^5 dynes cm^{-1} and the constant for the C $\leftrightarrow$ S linkage as 8×10^5 . The first of these is nearly identical with that obtained from carbon dioxide. The Raman spectra data from which these calculations were made are given in Table 59.

Table 59.—The Raman Shifts of Carbon Oxsulfide.

$\Delta\bar{\nu}$	i	ν
524	0	ν_2
678	00	
859	6	ν_1
1041	$\frac{1}{2}$	$2\nu_2$
1383	0	$\nu_1 + \nu_2$
2055	0	ν_2
2233	0	$2\nu_1 + \nu_2$

This compound should have three fundamental frequencies observable in the Raman effect, two of which are polarized and one depolarized. The symmetrical parallel oscillation ν_1 corresponds to the vibration of one of the end atoms against the rest of the molecule and this type of vibration is indicated by $\Delta\bar{\nu}$ 859. The ν_2 deformation vibration is presumably $\Delta\bar{\nu}$ 524 and ν_3 , the anti-symmetrical parallel oscillation, according to Dadiou and Kohlrausch, is $\Delta\bar{\nu}$ 2055. Some of the observed lines undoubtedly represent combinations. For example, a combination of ν_2 with ν_1 yields $\Delta\bar{\nu}$ 1383 and $2\nu_2 \approx 1048$ corresponding to the observed $\Delta\bar{\nu}$ 1041. Although

$\Delta\bar{\nu}$ 2055 is considered as the fundamental ν_3 , the magnitude of this shift, observed as an absorption band in the infrared, is $\Delta\bar{\nu}$ 2080, which is very close to twice the observed shift at $\Delta\bar{\nu}$ 1041. A combination of ν_1 with $\Delta\bar{\nu}$ 1383 yields 2242 which is not observed in infrared absorption. The weakest frequency at $\Delta\bar{\nu}$ 678 does not appear in the infrared and there is some question as to the reality of its existence. The C—S shift where the bond is a single one, as determined from the Raman spectra of the mercaptans, thioethers and similar organic compounds, occurs near $\Delta\bar{\nu}$ 650 and is very intense. If no other factors intervene this would give a calculated value of approximately $\Delta\bar{\nu}$ 1000 for the valence vibration of C=S, (comparing C—C and C—N with C=C and C=N). It seems quite probable, therefore, from the purely empirical chemical point of view, that the linkage between carbon and sulfur is a double-bonded one. It is to be remembered that the type of structure illustrated by $=C=$ causes a somewhat profound reduction in the normal double-bond frequencies in the allenes and isocyanates and probably in carbon dioxide.

Carbon Oxychloride

The Raman spectrum of carbon oxychloride or phosgene according to Henri and Howell⁷²⁵ consists of three lines, $\Delta\bar{\nu}$ 290, 444 and 567. This spectrum is incomplete, and since polarization and intensity data are also missing it is not possible to discuss these results in detail.

Hydrogen Sulfide

Gaseous hydrogen sulfide shows one strong Raman line at $\Delta\bar{\nu}$ 2615.^{134, 138} There is a notable decrease in the magnitude of this vibration in the liquid.^{134, 437}

According to Sirkar and Gupta,^{1475, 1481} solid hydrogen sulfide exhibits several Raman frequencies. These are $\Delta\bar{\nu}$ 2523, 2547, 2558 and a broad band which is present both as a Stokes and an anti-Stokes line at $\Delta\bar{\nu}$ 80. As hydrogen sulfide is a non-linear triatomic molecule with symmetry C_{2v} , it should have three Raman frequencies, ν_1 for the parallel symmetrical vibration, ν_2 for the parallel deformation vibration, and ν_3 for the asymmetrical perpendicular vibration. Of these three frequencies, as has been pointed out several times, ν_1 is generally the strongest. This corresponds to the line at $\Delta\bar{\nu}$ 2523. The ν_3 on the other hand corresponds to the doublet at $\Delta\bar{\nu}$ 2547 and 2558. No deformation vibration was observed. In the gaseous or liquid states only one frequency has been measured. The explanation given for this behavior is that when the bond angle becomes 90° ν_1 and ν_3 become identical. In the solid state the bond angle is changed just enough to cause a small separation of these lines. If it is assumed that $\Delta\bar{\nu}$ 2547 and 2558 correspond to ν_3 , an explanation must also

be given for this doubling. The appearance of the doublet instead of the single line due to the antisymmetric vibration can be accounted for by assuming that this vibrational level is split into two parts by the electric field of the crystal lattice. This would seem to indicate that the influence of intermolecular fields in the solid state is greater than in the liquid. It is this field which gives rise to the intermolecular vibration at $\Delta\tilde{\nu}$ 80. The calculation of the force constant for this compound in the solid state yields a value of 3.65×10^5 dynes cm^{-1} and a bond angle of 108° . This is somewhat less than the value found for k in the gaseous state.

The interrelation of the data obtained from hydrogen sulfide and other sulfur and carbon compounds of a somewhat similar nature is illustrated in Table 60 which gives the molecular constants calculated from the Raman effect.

Table 60.—Molecular Constants Calculated from the Raman Effect.

Substance	α^*	$s \times 10^8$ (cm.)	$k \times 10^{-5}$ (dynes per cm.)	$d \times 10^{-5}$ (dynes per cm.)
O=C=O	180°	0.98	13.7	1.2
S=C=S	180°	—	6.9(ca.)	1.5(?)
O=C=S	180°	O...C 1.04 C...S 2.38	13.6 8.0	0.4
O=S=O	120°	2.24	9.6	1.6
H—S—H	90°	1.43	3.9	0.02
S—H	—	1.35	3.8	—

* α = valence angle; s = interatomic distance from central atom; k = constant in dynes per centimeter; d = deformation constant in dynes per centimeter.

Phosphine, Phosphine-d-d₃ and Phosphorus Halides

Since phosphine, like ammonia, is supposed to have a pyramidal structure of symmetry C_{3v} , there should be four Raman frequencies: two parallel and polarized and two perpendicular, doubly degenerate and depolarized. Not all of these have been observed. Apparently the vibration near $\Delta\tilde{\nu}$ 2327^{468, 713, 1746} is the ν_1 vibration from intensity considerations. Delfosse⁴⁶⁸ considers this the same type of vibration as $\Delta\tilde{\nu}$ 3335 observed in ammonia. Hemptinne and Delfosse⁷¹³ observed a difference in frequency between the gaseous and the liquid states of approximately 20 wave numbers, the ν_1 oscillation for the liquid being $\Delta\tilde{\nu}$ 2305. Some of the deuterium derivatives have been investigated by these authors. The frequencies found are $\Delta\tilde{\nu}$ 1684 for the gas for the ν_1 vibration and $\Delta\tilde{\nu}$ 1664 for the liquid. In addition $\Delta\tilde{\nu}$ 807 and 740 were observed in the liquid where presumably $\Delta\tilde{\nu}$ 807 would be the ν_4 and 740 the ν_3 vibrations. For phosphine-d, ν_1 is given as $\Delta\tilde{\nu}$ 1825 and for phosphine-d₂ as $\Delta\tilde{\nu}$ 1755. The other observed frequencies for phosphine itself are 1121 and 990 corresponding to ν_4 and ν_3 respectively. If the latter frequency is corrected for an anharmonicity it becomes $\Delta\tilde{\nu}$ 1050. This yields a force constant of

3.16×10^5 dynes per cm^{-1} . These results are in reasonable agreement with those of Yost and Anderson¹⁷⁴⁶ who observed $\Delta\bar{\nu}$ 979(2), 1151(1) and 2306(10) for the liquid, corresponding to ν_3 , ν_4 and ν_1 respectively. As in ammonia the ν_2 frequency is extremely weak and is unobserved in the Raman effect.* It is concluded generally that the valence angle is approximately 96° or slightly less than that observed in ammonia. Howard⁷⁶⁰ comes to approximately the same conclusion.

Phosphorus trifluoride, although it has been investigated principally in the liquid form, is included here for the sake of comparison with phosphine. It is also mentioned under compounds of phosphorus. This substance has a regular pyramidal structure, according to Yost and Anderson,¹⁷⁴⁶ who find that the liquid yields $\Delta\bar{\nu}$ 486(3), 513(3), 840(10) and 890(10) for ν_4 , ν_3 , ν_2 , ν_1 respectively, where again ν_1 and ν_3 are parallel and ν_2 and ν_4 are perpendicular vibrations. The gaseous phosphorus trifluoride yields values quite close to those observed in the liquid with the exception of the absence of vibration corresponding to ν_4 . Phosphorus trichloride and tribromide follow the same pattern as described above. These results are summarized in Table 61.

Arsine and Arsine- d_3

Arsine, like phosphine or ammonia, is presumed to have a pyramidal structure and should therefore give rise to four Raman frequencies. Actually only three are observed. Delfosse⁴⁶⁹ records $\Delta\bar{\nu}$ 910, 990 and 2094. Of these, $\Delta\bar{\nu}$ 910 and 2094 correspond to ν_3 and ν_1 as symmetrical parallel vibrations, $\Delta\bar{\nu}$ 990 corresponds presumably to ν_4 , the lower frequency perpendicular vibration, and ν_2 is $\Delta\bar{\nu}$ 2185 according to Sutherland, Lee and Wu. Both ν_4 and ν_2 are doubly degenerate. Deuterium substitution does not cause a splitting of the degenerate frequencies in phosphine or arsine. Arsine- d_3 gives rise to only three observed frequencies, *i. e.*, $\Delta\bar{\nu}$ 630, 730 and 1508. Howard⁷⁶⁰ calculated the principal valence angle in arsine as 94° . His calculations of the vibrations of the pyramidal model are not in too good agreement with the observed frequencies.

It is to be understood that calculations of frequencies in arsine, phosphine, ammonia or other compounds from a theoretical point of view may or may not agree with the observed frequencies. In some cases the theoretical values have been made to equalize the observed frequencies by the introduction of as many as three, four or five constants into mathematical equations. In other cases, corrections due to anharmonicity or other factors are likewise introduced. From a chemical point of view this is somewhat reminiscent of the use of the activity coefficient to correlate

* Sutherland, Lee and Wu (unpublished results) record $\Delta\bar{\nu}$ 2423 for ν_2 .

experimental data with theoretical predictions. At times the use of these two corrective factors serves a constructive purpose in indicating possibilities, but in some circumstances their use is reminiscent of Bancroft's description of the "Gold Dust twins."

Diborane

The spectrum of liquid diborane (B_2H_6) contains an isotopic triplet $\Delta\tilde{\nu}$ 793, 806, and 821; a broad line at 1108 and an intense doublet at 2102 and 2523. Anderson and Burg suggest that the abnormally large force constants for the B—B, C—C and Si—Si bonds in diborane, ethane and silane are caused by forces associated with those which restrict internal rotation.

Chapter 21

The Raman Spectra of Phosphorus, Sulfur and Carbon

Phosphorus

Three elements—besides the common gases—whose spectra have been studied are phosphorus, sulfur and carbon. Bhagavantam¹²³ originally obtained from yellow phosphorus $\Delta\tilde{\nu}$ 374, 468 and 607. More recently Venkateswaran^{1624, 1632, 1633} has obtained from liquid phosphorus $\Delta\tilde{\nu}$ 363(2), 465(6), and 606(10). The first two of these shifts are completely depolarized, and the last shift has a depolarization factor ρ of 0.05. These shifts and their depolarization factors are in accord with the proposed tetrahedral model of Bhagavantam.¹²⁶ For the particular law of forces adopted by him, the frequencies should have the ratio $2:\sqrt{2}:1$. The fact that the observed frequencies deviate from this ratio is regarded as indicating that the force system in the molecule is more complicated than that assumed. The non-polar character of the P_4 group according to Venkateswaran¹⁶²⁴ is demonstrated by the small alteration in its spectrum with a change in the state of aggregation. The alteration in any of the frequencies observed does not exceed ten wave numbers in progressing from the solid to the vapor state, or in solution.

Besides the three vibrational frequencies recorded for phosphorus, Venkateswaran¹⁶²³ has noted also that the exciting line in liquid phosphorus is accompanied by a completely depolarized wing. This wing is replaced in the solid by a fairly sharp and intense line whose displacement is $\Delta\tilde{\nu}$ 36. The fact that no polymer higher than P_4 is known to exist eliminates the suggestion that this line may be due to intermolecular oscillations of polymerized groups. If it is assumed that this shift owes its presence to a vibration of the crystal lattice, the application of a modified formula of Lindemann for the calculation of this frequency leads to the following:

$$\nu = CR^{\frac{1}{2}}N^{\frac{1}{3}} \frac{T_m}{MV^{\frac{2}{3}}}$$

or

$$\nu = 0.77 \times 10^{12} \frac{T_m}{MV^{\frac{2}{3}}}$$

where T_m is the melting point, M the molecular weight, and V the molecular volume. In this case $T_m = 317$, $M = 124$, $c = 2.75$, $R^{1/2} N^{1/3} = 0.77 \times 10^{12}$ and $V = 70.66$ which leads to $\nu = 8.2 \times 10^{11}$ vibrations per second or $\Delta\bar{\nu} = 27.3$. This is in reasonably good agreement with the value $\Delta\bar{\nu} 36$, observed from the solids. Bhagavantam and Venkatarayudu have calculated the specific heat of phosphorus by using 12 Debye and 3 Einstein functions. The normal frequencies of the P_4 molecule were calculated by group theory methods.

Sulfur

Krishnamurti^{906, 909, 913, 914, 919} obtained four Raman lines from sulfur crystals when irradiated at liquid air temperature.⁵⁶⁹ He observed $\Delta\bar{\nu}$ 85(0), 151(4), 183(0), 214(4), 243(0), 430(0), 467(8) as a statistical average of the lines recorded by him. The three strongest lines are the same in the crystals as they are in a solution of sulfur dissolved in carbon disulfide. The shift reported at $\Delta\bar{\nu}$ 85, however, disappears on solution. Both the mercury line at λ 5461 Å and the cadmium line at λ 5086 Å were used as sources of excitation. Krishnamurti has attempted to explain the observed Raman shifts in terms of combinations of some of the fundamentals on the one hand, and, on the other, by the fact that there is a change in the polymerized form of sulfur on solution in carbon disulfide. Venkateswaran^{1620, 1632} has confirmed these observations and has added the information that no difference could be detected in the structure or position of the Raman lines in the liquid state and in the rhombic form of sulfur. In addition, however, there is a frequency recorded at $\Delta\bar{\nu}$ 114, which is not present in monoclinic sulfur, along with $\Delta\bar{\nu}$ 185, 243, and 434 recorded for rhombic sulfur. Whether this absence in the monoclinic form has any significance is undetermined. With a 50-per cent solution of sulfur in carbon disulfide the following values of the depolarization constant were obtained: for $\Delta\bar{\nu}$ 152 ρ approaches 6/7, for $\Delta\bar{\nu}$ 216 $\rho = 0.23$, and for $\Delta\bar{\nu}$ 470 $\rho = 0.08$. The shifts at $\Delta\bar{\nu}$ 85 in the liquid and $\Delta\bar{\nu}$ 434 in the solid are both depolarized, but the amount of depolarization was not accurately determined. The observed Raman shifts in sulfur agree quite well with the lines observed in infrared absorption where both lines and absorption bands are present.

There have been several proposed structures to explain the x-ray and infrared absorption data obtained from sulfur. One of these assumes that the unit cell consists of eight molecules of 16 atoms each, and that the S_{16} molecule consists of eight S_2 groups which are situated at the corners of a cube. Another view is that the unit cell consists of 16 S_8 molecules, and that each molecule contains eight atoms of sulfur which assume a symmetrical puckered ring structure. This ring is formed from two plane

squares (the sulfur atoms being at the corners of each square) one square being turned at an angle of 45° in respect to the other and situated at a short distance above it. Venkateswaran¹⁶³² also assumes two such squares, but adds the requirement that the neighboring atoms in the plane of each square are coördinately linked. In order to account for the strong infrared absorption observed, it is presumed further that one pair of sulfur atoms situated diagonally from each other at two of the corners of one square possess eight electrons while the remaining pair similarly situated, possess twelve. This in effect attributes a positive charge to one pair and a negative charge to the other, the individual atoms becoming quadrivalent. The intense and sharp line at $\Delta\tilde{\nu}$ 470 is attributed to the expansion and contraction of the squares constituting the molecule. The line at $\Delta\tilde{\nu}$ 150 which is depolarized, is attributed to the torsional oscillations of the two squares against each other. The $\Delta\tilde{\nu}$ 216, which is only partially depolarized, is also attributed to the oscillation of the two squares against each other.

This concept of two adjacent puckered rings consisting of four sulfur atoms each, the atoms in each ring being bound together by coördination valencies and bound between rings by homopolar linkages, has been used by Venkateswaran to explain the changes in properties of sulfur with temperature. It is presumed that as the temperature is raised the coördinate linkage gradually gives way and the molecules are more free to approach each other. Intriguing as this conception may be, it must be remembered that this is still largely speculative from a Raman spectra point of view. For that matter the same may be said of other methods of physical approach as applied to sulfur.

The Raman shift at $\Delta\tilde{\nu}$ 85, taken as the average shift, is considered by Venkateswaran¹⁶³³ to be a degenerate vibration of the crystal lattice which persists also in the liquid state. From Lindemann's calculations sulfur has a lattice frequency of 3×10^{12} vibrations per second which in wave numbers, gives $\Delta\tilde{\nu}$ 100. This formula, however, is only strictly applicable to cubic lattices. The difference between the calculated and observed values is evidently due to a difference in crystalline structure. Bhagavantam and Venkatarayudu have calculated the normal modes of vibration and frequencies of the sulfur molecule on the assumption that the eight atoms in the molecule occupy the corners of a puckered octagon. Of the eleven modes of vibration thus calculated, seven are found to be doubly degenerate and four are non-degenerate. Five of the former type and two of the latter are Raman active. These authors have also calculated the specific heat of sulfur by taking the sum of the Debye function and a number of Einstein functions associated with the various normal frequencies.

There is one other possibly significant fact which should be mentioned

in a discussion of the structure of molecular sulfur. It has been mentioned that the most symmetrical oscillations would correspond to the shift $\Delta\bar{\nu}$ 470, which is also the most intense vibration. The organic polysulfides also have a shift near this region. This appears at approximately $\Delta\bar{\nu}$ 485 and is relatively characteristic of the S—S type of binding. The structure of the organic molecules is undoubtedly different from that of sulfur. It would seem a reasonable presumption that in the organic molecules, particularly in the higher polysulfides, this portion of the chain would represent a bent-chain structure. It is possible that this part of the organic sulfur molecule may be somewhat similar to an equivalent portion of the sulfur molecule. It has been seen before that some characteristic types of linkage do not wholly depend on the configuration of the entire molecule but may, as a first approximation, be represented by the vibrations of a particular portion of the molecule wherein such vibration gives rise to a more or less characteristic frequency.

Carbon

Bhagavantam,^{123, 127, 130, 161} Nath,¹¹⁵⁸ Ramaswamy,¹²⁷⁹ Robertson¹³⁸² and Venkatarayudu (Raman Jubilee volume) have investigated the spectrum obtainable from diamonds. Each carbon atom is considered to be placed tetrahedrally to its four nearest neighbors (cf. SiO_4 ion). This arrangement should yield four Raman lines, of which one should be very prominent and polarized. This appears at $\Delta\bar{\nu}$ 1332 and is surrounded by some feeble components, $\Delta\bar{\nu}$ 1158, 1288, 1382, 1431, 1480 and 1585, whose origin is indefinite. Some of these may be combinations or overtones of an unobserved fundamental and others may appear because of the isotope effect. The $\Delta\bar{\nu}$ 1332 shift would correspond to a force constant greater than a single bond and less than a double bond if the simple harmonic formula is deemed applicable.

Chapter 22

The Raman Spectra of Water, Crystalline Hydrates, Bases and Hydrogen Peroxide

Fundamental Vibrations

The most consistently divergent results in any Raman spectra studies have been those obtained from the investigation of water. This is primarily attributable to the unique broadness of the bands observed. Theoretically, water vapor has three fundamental frequencies, namely, $\Delta\tilde{\nu}$ 1595 ($\delta\pi$) for the transverse oscillation or the bending motion of the hydrogen atoms, $\Delta\tilde{\nu}$ 3600 (ν_π) for their symmetrical oscillation in a linear direction along the line of the valence bonds, and $\Delta\tilde{\nu}$ 3757 (ν_σ) for the asymmetrical oscillation of the atoms in the molecules. Part of the difficulty has been that not all of these are active either in infrared absorption spectra or in Raman spectra. Further, from the latter point of view there appear possibly three bands in the $\Delta\tilde{\nu}$ 3400–3600 region for the liquid. These are not observable in the infrared absorption as the dipole moment change is small. On the other hand, $\Delta\tilde{\nu}$ 3756 is not observed at this frequency in the Raman spectra for either the liquid or vapor, but appears as $\Delta\tilde{\nu}$ 3630 in the liquid and 3654 in the vapor. The possible conclusion has been reached that the multiplicity of bands observed in liquid water owe their origin to the existence of several molecular species whose interaction gives rise to a perturbation of the normal frequency shifts. Whether or not they are physically distinct species or are the result of hindered rotation or translation is still unsettled. The effect, however, in either case is that the interaction between adjacent water molecules is far from negligible and there is a pronounced effect upon the Raman spectra. This is supported in no small degree by the existence of other Raman shifts in the frequency range between $\Delta\tilde{\nu}$ 60 and 1600, which cannot be accounted for by the vibrations of a classic oscillator of the type AX_2 .

High-Frequency Shifts for the Water Bands

The results obtained up to 1937 have been summarized in detail by Hibben^{729, 734} and Magat.¹⁰⁰⁹ The earlier work, principally by I. R. Rao, indicated three Raman frequencies in the region $\Delta\tilde{\nu}$ 3220, 3420, and 3630, corresponding to the symmetrical vibrations of the hydrogen atoms.

The exact maxima estimated by visual inspection by different observers varied over a range of 50 or more wave numbers. The advent of more accurate determinations by means of microphotometry has materially reduced the discrepancies.

Unfortunately from the point of view of simplicity of interpretation, neither the intensity nor the maxima of the bands $\Delta\bar{\nu}$ 3220–3630 remains constant. Both intensity and maxima are influenced by dissolved electrolytes and by temperature. I. R. Rao,¹³⁰² Meyer,¹⁰⁸⁹ and Ganesan and Venkateswaran⁵⁷⁷ early observed that an increase in temperature caused a diminution in the intensity of the $\Delta\bar{\nu}$ 3220 frequency and an increase for $\Delta\bar{\nu}$ 3630. The opposite effect has been observed in going from water to ice. The effect of solutes is generally somewhat similar to that of a temperature increase.^{291, 728, 1191} The evidence for the existence of a band at $\Delta\bar{\nu}$ 3630 is dependent mainly upon a very small break in the curves, concomitant with a marked shift in the position of the central band. It is difficult, therefore, to decide whether this is indicative of a change in the position of the maxima of the band or an augmentation in the intensity of the highest frequency. Early observers and more recently Magat¹⁰⁰⁷ failed to observe any band at $\Delta\bar{\nu}$ 3630. On the other hand, Carrelli and Cennamo³⁴² consider the principal water band to be made up of three components, $\Delta\bar{\nu}$ 3110, 3400, and 3590. The extensive work of I. R. and C. S. Rao^{1297, 1299, 1311, 1313} also indicates three bands. More recently Cross, Burnham, and Leighton³⁹² concluded that the three components making up the principal water band are $\Delta\bar{\nu}$ 3190, 3440, and 3650. These authors have investigated the effect of temperature up to 374° C. There is no doubt about the gradual approach of the principal maximum toward $\Delta\bar{\nu}$ 3600, the ν_* symmetrical oscillation, as the temperature exceeds 100° C. This is confirmed by Ukholin.¹⁵⁹⁶

Low-frequency Shifts for the Water Bands

Hibben,⁷³⁴ Segré,¹⁴²² Bolla,¹⁸⁴ Magat,^{1006, 1009} and Cross, Burnham, and Leighton³⁹² have indicated frequencies less than $\Delta\bar{\nu}$ 1600. Some of these are $\Delta\bar{\nu}$ 60, 140–172, 510–780. From the published microphotometric curves the frequencies of $\Delta\bar{\nu}$ 60 and 780 are very doubtful, as will be seen later. Nevertheless it is of considerable importance to confirm the existence of these and other frequencies mentioned, and this has been done by Hibben.⁶⁰⁹ There is no doubt that low-frequency oscillations do exist at $\Delta\bar{\nu}$ 170 and 500. This is likewise true of $\Delta\bar{\nu}$ 2170, the last frequency having been noted before only by Bolla,¹⁹¹ Magat,¹⁰⁰⁹ and Cross, Burnham, and Leighton.³⁹² Owing to their extreme weakness none of the frequencies below $\Delta\bar{\nu}$ 3220 was observed with accuracy until the advent of ultraviolet excitation, although it was postulated²⁹¹ that a frequency at $\Delta\bar{\nu}$ 1600 should

exist; and indeed it was early observed by Kimura and Uchida⁸⁰⁹ and by da Silveira.¹⁴³³ The $\Delta\bar{\nu}$ 500–700 band is claimed by Magat¹⁰⁰⁸ to show an anomalous disappearance at 37° C. This is disputed by Bolla¹⁹⁴ and by Hibben.⁷³⁴

Other shifts supposedly observed are $\Delta\bar{\nu}$ 3990,¹⁹¹ 984,⁷⁸² 2355,⁵⁷⁷ 4023 and 5100,¹⁰⁰⁷ and a group reported by Hulubei⁷⁷⁰ extending from 6747 to 10944, but these are doubtful.

It has been suggested by I. R. Rao and Koteswaram¹³¹⁶ that some of these frequencies, as well as the two shifts $\Delta\bar{\nu}$ 170 and 500, are attributable to a wrong assignment of exciting frequencies and that these shifts are in reality the $\Delta\bar{\nu}$ 3400 band excited by different mercury lines. Although in some cases this may be true, it is certainly not the case for $\Delta\bar{\nu}$ 170 and 500, since Hibben⁷³⁷ has shown that in the type of mercury arc employed by him there is no mercury line of a frequency higher than λ 2537 capable of giving rise to any Raman lines. Furthermore, Cartwright³⁴⁷ has unequivocally demonstrated that both of these frequencies are present in the infrared absorption of both ice and liquid water.

Ananthakrishnan^{21, 28} has made a special study of the 160–175 shift in both water and water-d₂. The frequencies near $\Delta\bar{\nu}$ 3230, 3430, and 3600 are shifted to $\Delta\bar{\nu}$ 2360, 2515, and 2662 in water-d₂.¹³¹⁷ The δ_r oscillation is similarly shifted from $\Delta\bar{\nu}$ 1650 to 1235 and only the lowest frequency observed, $\Delta\bar{\nu}$ 175, remains constant. This is further confirmatory evidence of the existence of the lower frequency shifts. As has been mentioned already, these have been ascribed to hindered translation and hindered rotation. The constancy of $\Delta\bar{\nu}$ 160–175 in both normal and heavy water is strong evidence that this frequency is relatively independent of the hydrogen atoms and must therefore be due to an intermolecular change. The infrared absorption also confirms the constancy of this frequency in these two compounds. The $\Delta\bar{\nu}$ 500 probably has been correctly ascribed to a hindered rotation of the hydrogen atoms.

Various explanations have been offered for both the appearance of these low frequencies and for the shifts in the maxima of the larger wave number shifts. I. R. Rao has consistently ascribed the variations in the bands adjacent to $\Delta\bar{\nu}$ 3400 as due to a change in the proportions in which the water polymers, *i. e.*, H₂O, (H₂O)₂ and (H₂O)₃, are present and he has ascribed to the frequency near $\Delta\bar{\nu}$ 3600 the unpolymerized water. Bernal and Fowler have proposed a quasicrystalline arrangement for water having respectively a tridymite, quartz, and close-packed ideal structure as a function of increasing temperature. The difference between these concepts is more illusory than real. The essential fact is that there is a profound influence on the Raman spectrum of water as changes in the constitution of water take place. Furthermore, the lower frequency shifts can be

explained only on the basis of an intermolecular action of such intensity that the forces thus brought into play give rise to unusual Raman shifts. It is highly probable that whatever condition exists is an equilibrium condition and is rather a continuing structure in the liquid than a specific grouping of molecular aggregates of definite size.

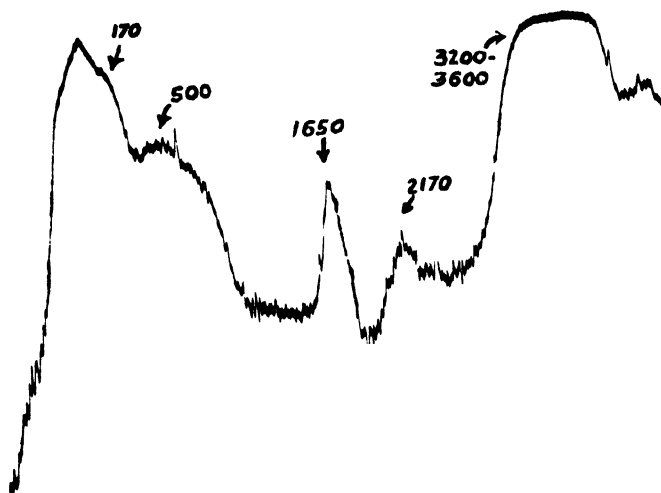


FIGURE 50. The Raman Bands of Water.

In Figure 50 is shown the Raman spectrum of water, indicating all these bands under discussion, and Figure 51 is an enlarged microphotometric tracing of the $\Delta\tilde{\nu}$ 160-175 band to indicate the reality of its existence. It is to be noticed that there is an additional frequency at $\Delta\tilde{\nu}$ 2150 which has not been touched upon as yet. This band is probably the result of a combination of $\Delta\tilde{\nu}$ 500 with $\Delta\tilde{\nu}$ 1650.

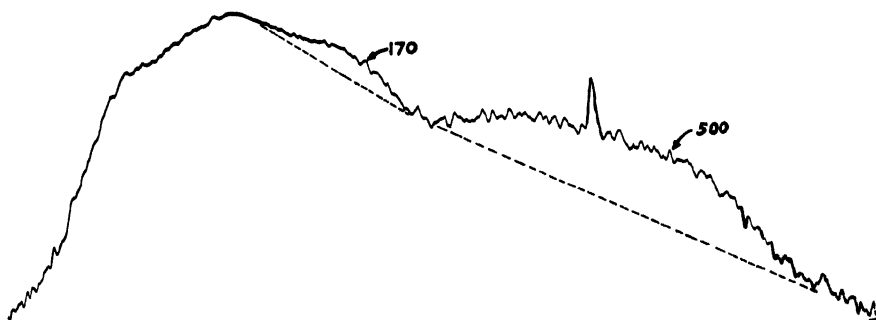


FIGURE 51. A Microphotometer Tracing of the Intermolecular Water Band. ($\Delta\tilde{\nu}$ 160-175).

Thus far the origin of various water bands has been discussed. The next problem is to consider in more detail the influence on these bands of solutes, temperature, and polarization.

The polarization of Raman bands in ordinary water has been studied by Ananthakrishnan,²⁸ Ramaswamy,¹²⁸² Cabannes and Rousset,³³⁰ Cabannes and de Riols,³²⁶ and I. R. Rao.¹³¹⁵ The results of these investigations are conflicting. The work of Ananthakrishnan is reported without prejudice as to the accuracy of his results. According to this author the principal water bands are depolarized in the order of increasing frequency. In order to interpret these results it might be pointed out that the depolarization rules in Raman scattering give the depolarization factor of zero to less than 6/7 for any symmetrical and degenerate modes of oscillation, and approximately 6/7 for asymmetrical vibrations. Thus in the case of water the Raman band corresponding to ν_o should be highly depolarized and those corresponding to ν_r and δ_r should show a lesser degree of depolarization. Furthermore, it may *possibly* be reasonable to conclude that δ_r should be more depolarized than ν_r . This means that the depolarization factor ρ is greater for the antisymmetrical vibrations and less for the symmetrical ones. From the point of view of water vapor it has been mentioned already that ν_o corresponds to the asymmetrical oscillation and ν_r to the symmetrical one at $\Delta\tilde{\nu}$ 3600. In the liquid state if depolarization in the order of increasing frequency takes place, the shift at $\Delta\tilde{\nu}$ 3220 should correspond to the ν_r oscillation and $\Delta\tilde{\nu}$ 3430 to the ν_o . Finally δ_r should be more depolarized than the other frequencies. This seems to be in accord with the observations of Ananthakrishnan, but other workers believe that the ν_r frequency corresponds to $\Delta\tilde{\nu}$ 3600. The bands at $\Delta\tilde{\nu}$ 175, 500, and possibly 750 are also highly depolarized in normal water. Also the band at $\Delta\tilde{\nu}$ 175 has a depolarization value according to the maximum depolarization constant 6/7 in either water-d₂ or normal water.

The influence of temperature is to increase the maxima of the water bands between $\Delta\tilde{\nu}$ 3200 and 3600. This is shown in Figure 52 which indicates the shifting of the maximum as a function of temperature. Cross, Burnham, and Leighton³⁹² have investigated in detail the highest-frequency Raman displacements. There is no doubt from their figures of a wave number shift from near $\Delta\tilde{\nu}$ 3400 to 3600 as the critical temperature is approached. Neither is there any doubt of a shift of the maximum in the opposite direction in ice to approximately $\Delta\tilde{\nu}$ 3140, as observed by Hibben.⁷³⁴ As has been mentioned, however, there still seems to be a question as to the simultaneous existence of all these frequencies in the case of water. According to Cross, Burnham, and Leighton³⁹² a double frequency corresponding to two types of symmetrical 2-coördination would occur at near $\Delta\tilde{\nu}$ 3425 and would account for the Raman band at $\Delta\tilde{\nu}$ 3440. The

lower frequency is attributed to a 4-coördination maximum at $\Delta\bar{\nu}$ 3200, and the highest frequency near $\Delta\bar{\nu}$ 3600 to free water molecules. The measurements near the critical temperature, therefore, correspond to scattering due predominantly to single molecules. The hydrogen bond is presumably the binding unit between these molecular complexes. The fact that such complexes can exist is shown by the results of Hibben⁷³⁴

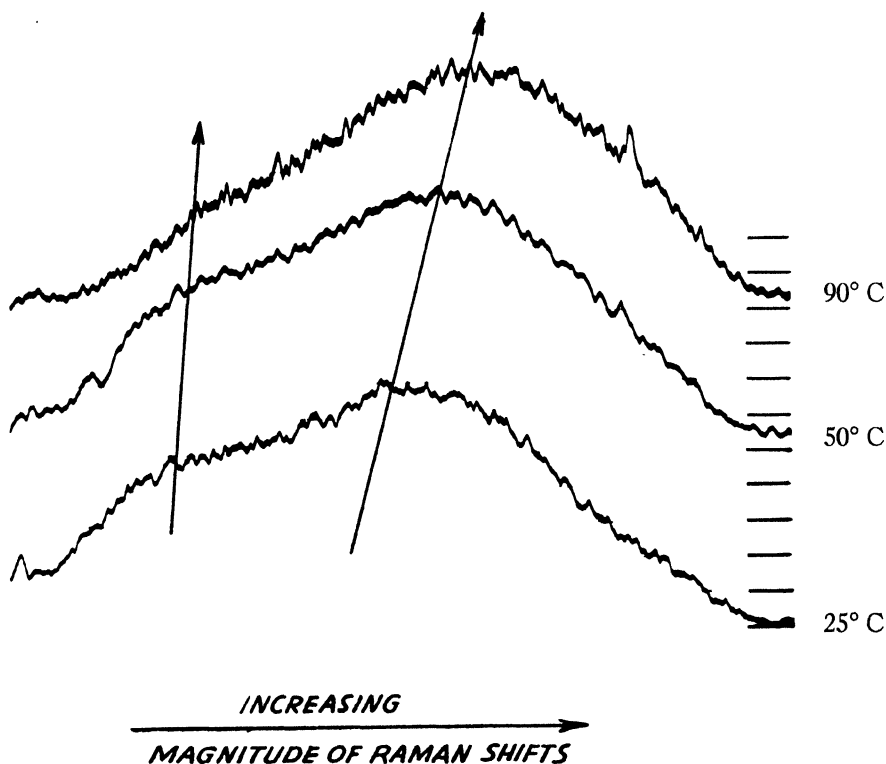


FIGURE 52. The Effect of Temperature on the $\Delta\bar{\nu}$ 3200-3600 Water Band.

in the study of aqueous solutions and particularly of ice, in which the lower-frequency oscillations due to the hindered rotation and translation are strongly in evidence. These are depicted in Figure 53 which, compared with the preceding figure, indicates their intensification as a result of the well-known intermolecular interaction in solid water (ice I, ice II, etc.).

Sutherland's¹⁵²³ observations with ice at -183°C . indicate a further shift to a lower Raman frequency, $\Delta\bar{\nu}$ 3030, of the $\Delta\bar{\nu}$ 3130 band which appears in ice near room temperature, and it possibly indicates fairly complete 4-coördination at liquid air temperatures. At 0° the other two

bands $\Delta\bar{\nu}$ 3277 and 3350 should perhaps be assigned to 2- and 3-coördination respectively. I. R. Rao ¹³¹¹ has consistently argued in favor of the classic $[\text{H}_2\text{O}, (\text{H}_2\text{O})_2, (\text{H}_2\text{O})_3]$ concept of water and has pointed out the variation in intensity of the water bands with temperature. This concept appears to be somewhat too well defined. On the other hand, it is often too easy to explain departures from the normal on the basis of hydrogen bonding or resonance. These explanations may err in the opposite

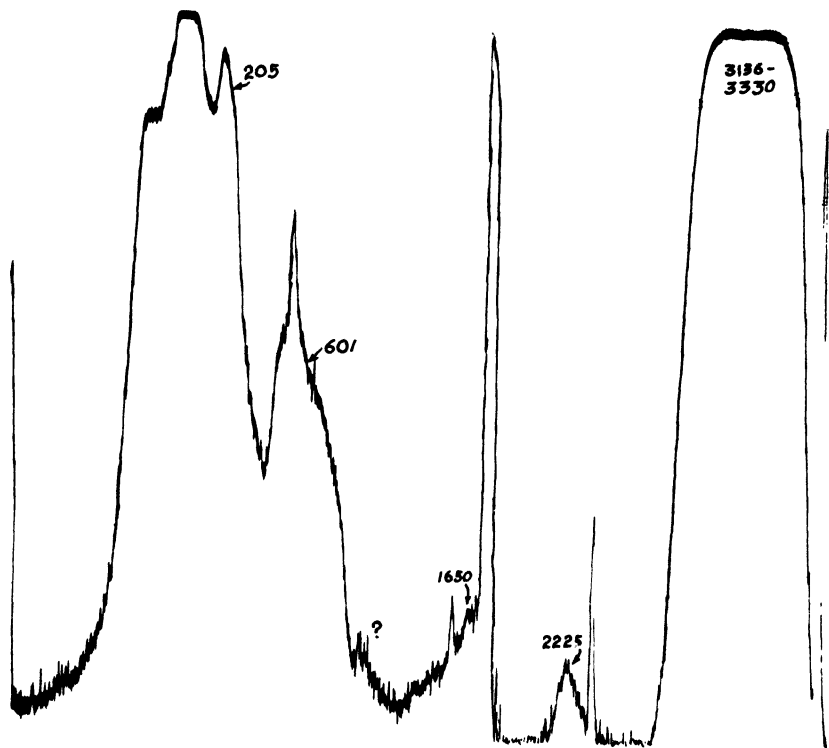


FIGURE 53. The Raman Spectra of Ice Showing the Enhancement of the Translational and Hindered Rotational Water Bands. (Cf. Figure 50.)

extreme. Neither concept is in contradiction to the experimental observations upon which ultimately any explanation must be founded. In any case the formula H_2O given water or ice is undoubtedly incorrect. Other factors, which are due to intermolecular interaction and influence both the physical and chemical properties of water, intervene. Evidence as to the nature of these factors and their magnitude obtained from Raman spectra illustrates an important application of this method of attack on the structure of liquids.

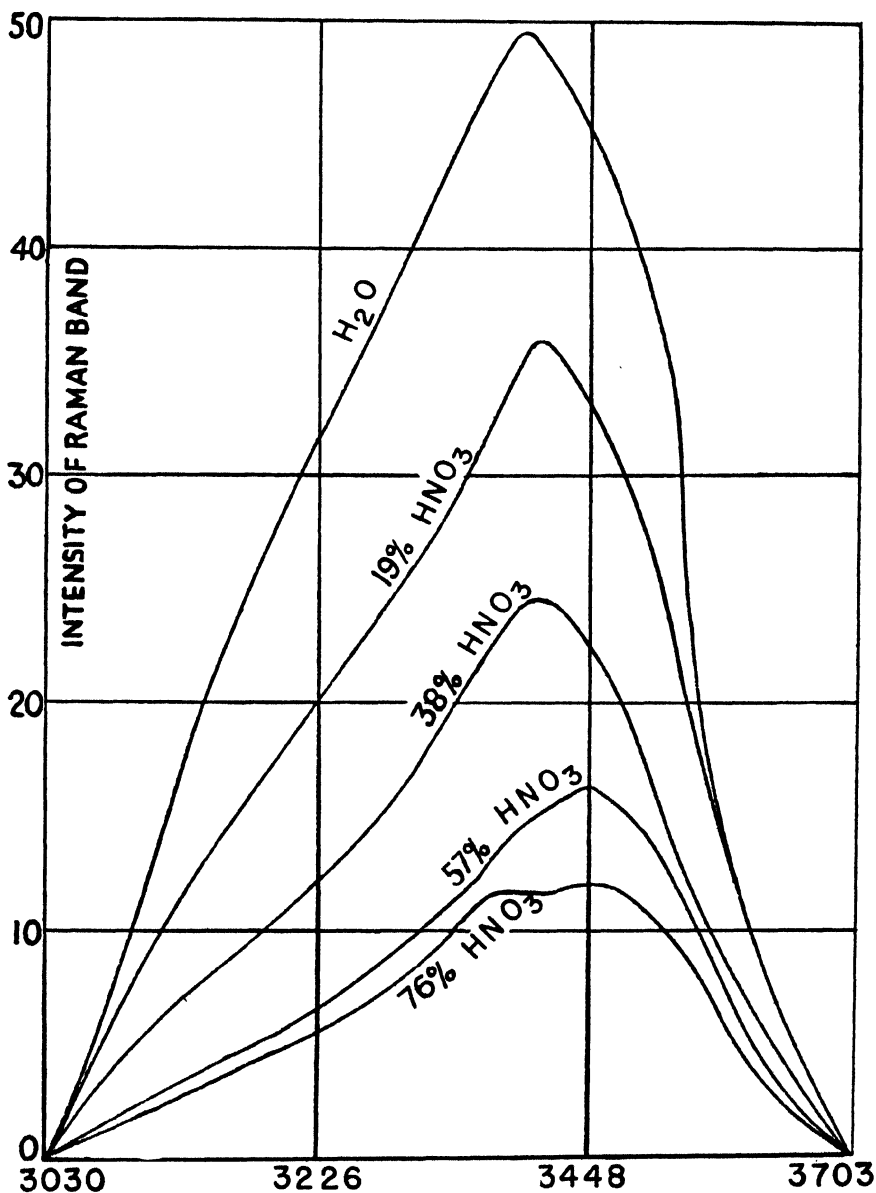


FIGURE 54. The Effect of Nitric Acid on the $\Delta\bar{\nu}$ 3200-3600 Water Band (after I. R. Rao).

The effect of solute action on the water bands has been investigated already by Hibben,⁷²⁸ I. R. Rao,¹³⁰⁸ and Kujumzelis, although this effect has been extensively investigated by infrared absorption. Until recently most of the work has been confined to the effect on the $\Delta\bar{\nu}$ 3200–3600 bands. In Figure 54 is shown the effect of increasing concentrations of nitric acid on these water bands, as studied by Rao. This shows a splitting of this band into at least two components and a shifting to the higher Raman frequencies. A similar sharpening of the water band was observed by Rafalowski¹²⁶⁴ in nitric acid solutions and solutions of potassium chloride. Hibben⁷²⁸ and Leighton and Burnham⁹⁷⁷ have investigated the effect of zinc chloride on the higher frequency band. It is contended by the latter authors that the short frequency component disappears on the addition of zinc chloride. This indicates a depolymerization of the solvent. Kujumzelis has studied the effect of halogens, nitrates, chlorates, perchlorates, iodates, sulfates and carbonates on the water bands. The most pronounced effect on the intermolecular bands is caused by the iodates. It is also contended that the effect of temperature is radically different from the effect of electrolytes. Landsberg and Malyshev have found that the dilution of water with dioxan has much the same effect on the spectrum of water as an increase in temperature, but with pyridine the position of the maximum of the water band remains unchanged.

More recently, the advent of ultraviolet excitation has added to the study of the lower frequency bands occurring in water. These were originally observed by Segré. Since the presumption is that the effect of solutes on all water bands is a change in the molecular or crystalline structure of the solvent, the lower frequency bands would be more sensitive to a modification than the extremely broad band occurring as a function of the O—H vibration. The effect of lithium chloride, magnesium chloride, potassium bromide, and sodium hydroxide on these low-frequency oscillations has been investigated by Hibben.⁷³⁴ Within the limits of the experimental error involved in quantitative measurements of such effects, there is no obvious change in the water bands as the result of the interaction of halides and water itself. This is also true of hydrochloric acid. However, the addition of alkali in the form of sodium hydroxide or barium hydroxide obviously diminished the intensity of the low-frequency shifts. The very existence of these shifts can be attributed solely to intermolecular interaction. Apparently, therefore, the function of the hydroxyl ion is to decrease polymerization rather than to increase hydration. Furthermore, a small number of hydroxyl ions are capable of depolymerizing a large number of water molecules. The effect of lowering the structural temperature of the solution by ions of small radii, as postulated by Bernal and Fowler, is therefore not realized. The persis-

tence of the frequencies whose origin is attributed to intermolecular effects in these solutions does not point to any pronounced dissociation of the structural complex with large ions, or any pronounced increase in the regularity of arrangement with small ions, as is shown in the accompany-

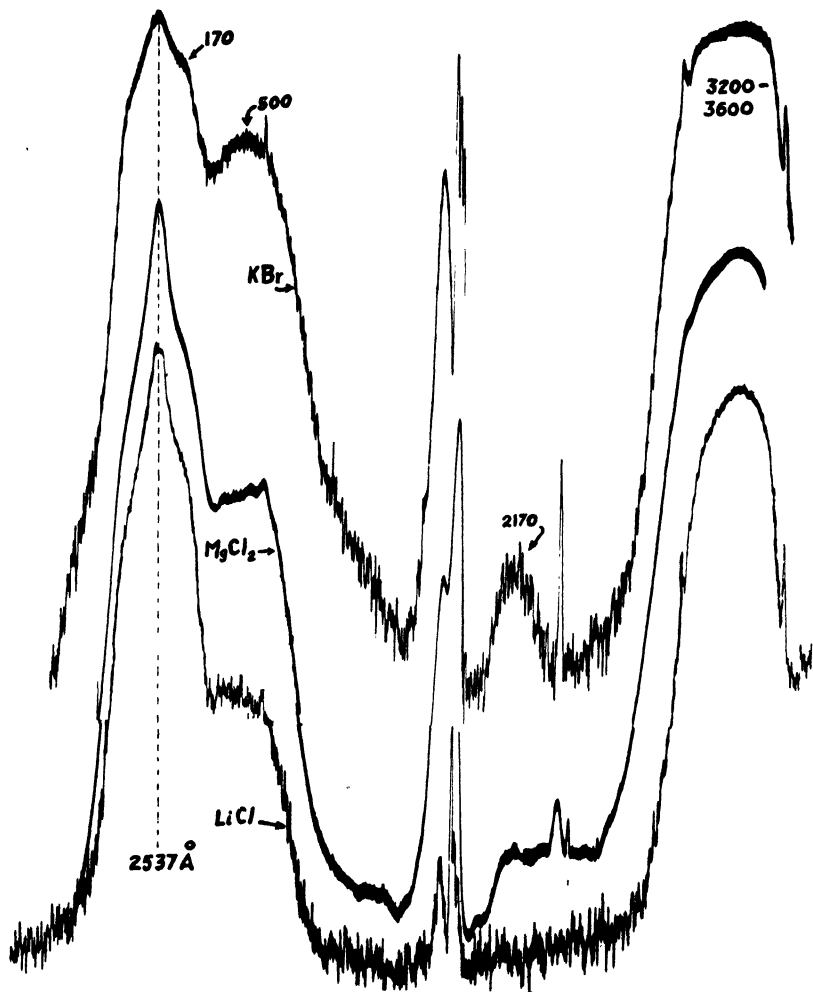


FIGURE 55. The Low-frequency Raman Shifts of Water in the Presence of Different Solutes.

ing Figure 55. This does not preclude the existence of small changes in structural temperature or arrangement beyond the sensitivity of the Raman effect. The alteration in the spectra of solutes in aqueous and other solutions will be discussed in a separate chapter.

Little has been said about the Raman spectrum of water-d₂ or water-d. The earlier work of Wood¹⁷¹³⁻¹⁹ was for the most part carried out with such impure samples of heavy water that the results are inexact from any quantitative point of view. Rank, Larsen, and Bordner¹²⁹⁰ have observed $\Delta\bar{\nu}$ 2666 for water-d₂ and 2718 for water-d in the vapor state. Bauer and Magat¹⁰⁷ have observed for water-d₂ $\Delta\bar{\nu}$ 170, 350, 500, 1207, 2389, and 2509. These correspond to $\Delta\bar{\nu}$ 176, 500, 700, 1659, 3221, and 3435 observed in ordinary water. The $\Delta\bar{\nu}$ 2389-2509 is a doublet and not a triplet. From this it is noted that $\Delta\bar{\nu}$ 170 remains unchanged and that $\Delta\bar{\nu}$ 350 and 500 have been shifted presumably from $\Delta\bar{\nu}$ 500 and 700, although thus far we have more or less ignored $\Delta\bar{\nu}$ 700 as being doubtful. Ananthakrishnan's^{20, 21, 28} results have already been discussed. He reports $\Delta\bar{\nu}$ 2363, 2515, and 2662. In addition to the frequency near $\Delta\bar{\nu}$ 1235 he observes a feeble companion at about $\Delta\bar{\nu}$ 1125. The $\Delta\bar{\nu}$ 1235 is the frequency which ordinarily occurs near $\Delta\bar{\nu}$ 1645 in normal water. These results indicate that the shifts in the spectrum are primarily mass effects and that there is little change in the force constant in going from water to water-d or water-d₂.

Water of Crystallization

In the discussion dealing with liquid water it was pointed out that the Raman shift corresponding to the ν_r oscillation was $\Delta\bar{\nu}$ 3600 but that at ordinary temperatures this is one of the weakest Raman shifts. The reality of this shift is demonstrated by the effect of temperature.³⁹² Actually there are two other Raman bands, near $\Delta\bar{\nu}$ 3200 and 3450, both of which are involved in the O $\leftrightarrow$ H oscillation in water. It has been shown also that in ice these are materially altered and are reduced to near $\Delta\bar{\nu}$ 3150 and 3350. In aqueous solution there is also a pronounced effect on the water bands, depending on the solute; the net effect, which depends on the particular solute, is generally to enhance the intensity of the band near $\Delta\bar{\nu}$ 3450.

In water of crystallization the same O $\leftrightarrow$ H frequencies are very much sharper than those observed with water and give rise to maxima which can be measured with a higher degree of accuracy. This does not, however, explain the entire results obtained with water of crystallization. In the latter case as many as four or five different bands or lines have been observed, all of which are reasonably sharp and whose maxima can be determined. These results are shown in Table 62. The recorded data on this table can be attributed largely to the observations of Nisi,¹¹⁷⁹ Ananthakrishnan³⁹ and Hibben.⁷³⁴ Canals and Peyrot, and particularly Nayar (Raman Jubilee volume) have also contributed extensively to this subject. The first point which is obvious on consulting this table is that the O—H oscillation is not greatly dependent upon the degree of hydration, since

there is no marked change in many cases in going from one molecule of water of hydration to ten. On the other hand, there is a certain degree of similarity between the recorded Raman shifts and those observed from pure water. In the crystal hydrates the water band near $\Delta\bar{\nu}$ 3200 is apparently shifted to a slightly higher value, namely, approximately $\Delta\bar{\nu}$ 3250. However, there is no Raman shift recorded in the region of 3650, in consequence of which, in a general sense, one may conclude that this vibration is probably reduced to a region corresponding to 3600. Even so, there are a few compounds which possess the Raman frequency shifts in the hydrates which have displacements in this particular region. In contradistinction to this, there are a number of hydrates which exhibit frequencies near $\Delta\bar{\nu}$ 3380 corresponding to a shift which does not exist in pure water vapor. Some authors argue that the principal lines observed in the crystal hydrates correspond to different polymerized forms of these water molecules. As more complete investigations of these crystal forms have continued it has been shown that there are not simply three lines in many cases, but four or five lines, which would tend to make untenable the allocation of particular water complexes to specific lines. In the earlier days of Raman spectra investigations of the crystal hydrates, often only one or two lines were observed; but, as improvements in technique have progressed, it is becoming more and more demonstrable that the number of lines obtainable from crystal hydrates may increase. On the other hand, it can be shown equally that, for example, in magnesium chloride hexahydrate there are apparently only two Raman lines in this region, and in cadmium sulfate eight-thirds hydrate there are only two lines. These shifts are illustrated in Figure 56. Contrary to these examples there exist at least three O—H Raman lines in sodium tetraborate tetrahydrate (see Figure 69, p. 434). One of the differences between the hydrates is the occasional lopping off of the frequency near $\Delta\bar{\nu}$ 3600 which has been ascribed to vibration of an unassociated water molecule. In the nitrates, from magnesium nitrate to bismuth nitrate, there are four discernable frequencies in the region corresponding to the water of crystallization. On the other hand, in the sulfates and halogen compounds there are chiefly three frequencies. In contradistinction to this it should be mentioned that other compounds, such as sodium carbonate decahydrate, exhibit an extremely broad band extending from 3150 to 3600 wave numbers. Sodium phosphate, dodecahydrate, exhibits an extremely broad band at 3150 to 3450 which is followed by a strong line whose frequency is near $\Delta\bar{\nu}$ 3650. This behavior is analogous to the dodecahydrate of sodium vanadate. Cabannes has recently noted that the number and polarization of the Raman water lines from gypsum are a

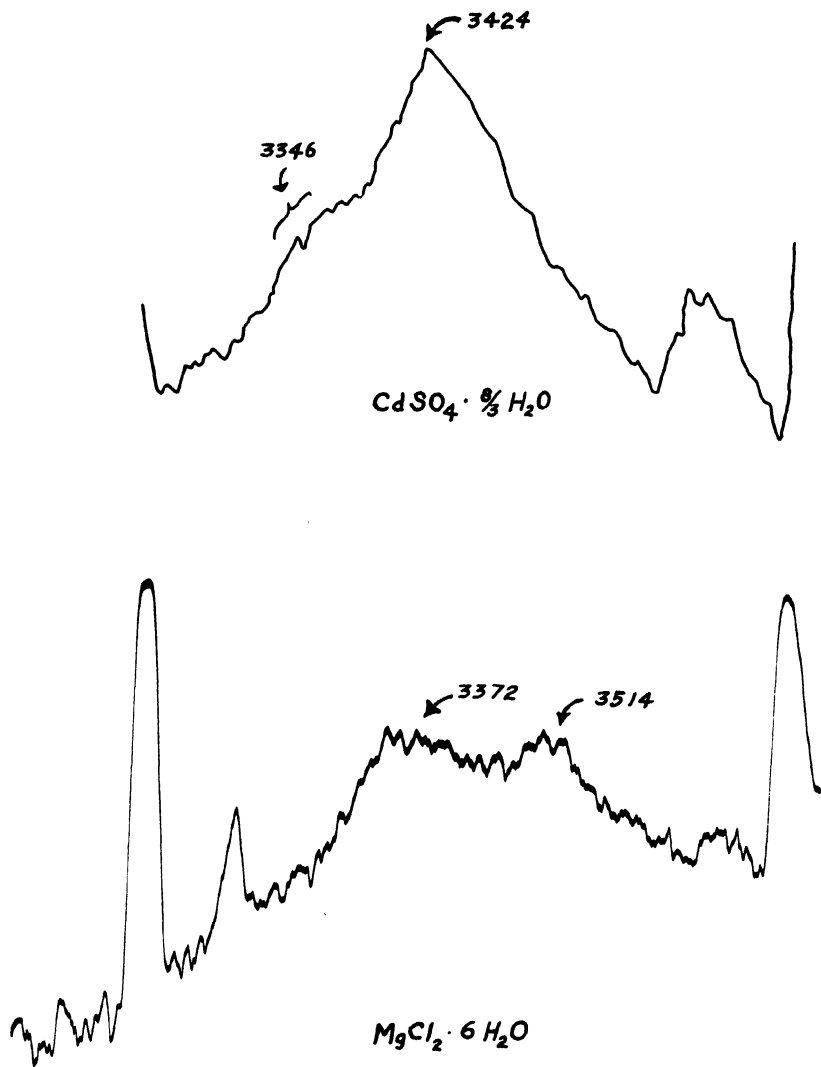


FIGURE 56. The Raman Water Bands Between $\Delta\bar{\nu}$ 3200-3600 from the Hydrates of Cadmium Sulfate and Magnesium Chloride.

function of the orientation of the binary axis of the crystal with reference to the incident ray.

From the published data it is difficult to fix any correlation between the number or the magnitude of the Raman spectra frequencies of the crystal hydrates and any other property of the molecules involved, par-

ticularly because a number of these observations were made at a time when quantitative examination was impossible. There is little doubt but that in time a correlation may be made between the ionic radii of the cation or anion or some other properties of the molecules which will lead to a relation between the magnitude of the Raman shifts for the hydroxyl groups and the chemical properties of the molecule. The only conclusion which can be adopted at the moment is that the cations have a very definite influence upon the Raman shifts of the O—H group in water of crystallization. This effect is equally noticeable in the case of the effect on the Raman shifts of the water bands in solution as a function of the solute. It should be remarked in passing that the frequency shift observed for the O—H group in the hydroxide, such as potassium hydroxide, occurs near $\Delta\tilde{\nu}$ 3610 which again is a first approximation to the oscillations expected from a free O—H group.

These values should be compared also to the O—H groups observed in various types of acids such as sulfuric acid, nitric acid, phosphoric acid, etc. On the whole it may be noticed that the O—H frequency in the acids is very broad as compared with those of the crystal hydrates and the magnitude of the frequency shifts is considerably lower than is observed with potassium hydroxide or other hydroxides. It is also lower than the frequencies observed in pure water. In most of the strong acids the O—H band, as observed, begins¹⁶³⁸ near $\Delta\tilde{\nu}$ 3000 or 3100 and extends to near $\Delta\tilde{\nu}$ 3300.

Bases

Krishnamurti⁹¹¹ found that crystalline sodium hydroxide gives a strong and sharp line at $\Delta\tilde{\nu}$ 3630 in reasonable agreement with the expected frequency from an O—H group in a water molecule. Most other observers have worked with the spectrum of sodium hydroxide or equivalent hydroxide in solution. This is undesirable because of the overlapping of the R—OH and H—OH shifts. However, there may be some enhancement in the general spectra which may lead to utilizable results. Woodward¹⁷³⁰ obtained in 12*N* sodium and potassium hydroxide solutions $\Delta\tilde{\nu}$ 3615, together with a strong continuous spectrum also observed by Bär.⁹⁷ This line is broad and diffused and comparable with the value $\Delta\tilde{\nu}$ 3603 observed by Nielsen¹¹⁷⁰ and by Thompson and Nielsen.¹⁵⁶¹

The amount of this shift is of the same general order of magnitude as that attributed to the $O \leftrightarrow H$ vibrations in methyl alcohol, $\Delta\tilde{\nu}$ 3380, or in ethyl alcohol, 3420. This diminution is not unusual since it is to be remembered that $O \leftrightarrow H$ frequencies in the case of the acids, water, ice, and water of crystallization, all differ depending on the constituents of the molecule. It is true also that in aqueous solution the modification of the

hydroxyl line is dependent upon the type of the solute, and in the crystal hydrates is a rough function of the cation. Nielsen concludes that it is not improbable that $\Delta\bar{\nu}$ 3603 observed in water and in the hydroxides belongs to the O—H ion and that the great width of the ordinary band is related to the hydration of these ions in water.

Hatley and Callihan⁷⁰² obtained three bands for water, namely, $\Delta\bar{\nu}$ 3228, 3435, and 3624 and studied the displacement of these bands as a function of sodium and potassium hydroxide concentration. The alkali concentration was varied between approximately 1*N* and slightly greater than 10*N*. It was observed in both cases that with increased concentration the center of gravity of the water bands shifted to the higher frequency, that is, 3624 which becomes much stronger with increasing concentration of alkali. The inference is that the water and hydroxyl bands are practically identical; particularly is this so with reference to the highest bands observed for water.

It has been tentatively suggested by Carrelli, Pringsheim and Rosen³⁴⁴ that one of the lines observed in ammonium hydroxide solution, namely, $\Delta\bar{\nu}$ 3385, might be attributed to the O—H ion. This is problematical. Woodward contends that it is more likely that this frequency is to be attributed to an undissociated O—H group rather than to the ion.

Hydrogen Peroxide

This compound has been written for many years as H_2O_2 . This formula gives only the ratio of hydrogen and oxygen and depicts nothing of its structure, which is necessary to explain its chemical and physical behavior. Investigations of the Raman spectrum of hydrogen peroxide, which have been few in number, have not solved completely the problem of the structure of hydrogen peroxide, but they have added to our knowledge of this problem.

The earliest comparisons were, of course, with water and in aqueous solutions. These demonstrated that there were other frequencies present in hydrogen peroxide which could not be attributed to the O—H vibrations—although for obvious reasons any investigation in moderately dilute solution could never be clear-cut so far as O—H vibrations were concerned.

The simplest approach is to consider hydrogen peroxide as a linear molecule similar to acetylene having the symmetry $D_{\infty h}$ and giving rise to three Raman lines, two polarized and one depolarized. Actually Venkateswaran¹⁶¹⁷ has observed $\Delta\bar{\nu}$ 875(8) and 903(2) under circumstances which did not permit any O—H vibrations to be observed.

Since then Simon and Fehér¹⁴⁸⁷ have studied the effect of a change in hydrogen ion concentration on the Raman spectrum of H_2O_2 . They conclude that not only is there a loosening of the O—O bond on neutralization with

sodium hydroxide but a dissociation to an $\text{H}^+[\text{HO}_2]^-$ configuration. These authors and Fehér⁵⁴² have observed shifts at approximately $\Delta\bar{\nu}$ 877, 1420, and 3400. The intensities of two of these lines are a function of concentration since both $\Delta\bar{\nu}$ 1421 and 877 decrease in intensity on dilution from 99 per cent hydrogen peroxide to 37½ per cent. The O—H band is quite broad. From these and other considerations it is postulated by these authors that the deformation vibration is represented by $\Delta\bar{\nu}$ 1420, in contrast to the frequency at $\Delta\bar{\nu}$ 1640 observed with water, and that a nonlinear molecule may be indicated with the two hydroxyl groups twisted at a 90° angle from each other. In an alkaline solution $\Delta\bar{\nu}$ 877 becomes very much weaker, while in an acid solution it is strongest.

In hydrogen peroxide- d_2 the $\Delta\bar{\nu}$ 3400 of hydrogen is converted to 2510, and $\Delta\bar{\nu}$ 1406 is converted to 1009. This is not in agreement with the linear representation of the molecular structure wherein the $\Delta\bar{\nu}$ 875 would represent the ν_b type of vibration corresponding to the motion of the O—H groups perpendicular to the axis of the molecule and out of phase. The $\Delta\bar{\nu}$ 3400 would be the symmetrical valence vibration (ν_2) of the O—H group, and the ν_1 ($\text{HO} \leftrightarrow \text{OH}$) motion is represented by $\Delta\bar{\nu}$ 1406. If this view were correct ν_1 would be little affected by deuterium substitution.

The only bent model of hydrogen peroxide which will yield but three fundamental Raman lines is the symmetrical zigzag configuration.

Polarization measurements on the Raman shifts would be of decided advantage in interpreting the structure of hydrogen peroxide. It is believed, nevertheless, that the present information implies a bent configuration which does not differ widely from the true one.

Chapter 23

The Raman Spectra of Halogen Compounds

Halides of the Type AX_2

Halogen compounds having the symmetry $C_{\infty h}$ and composed of molecules whose constitution may be designated by AX are principally confined to the halogen acids, such as hydrochloric acid. These are considered in detail under the acids. Other halogen compounds of the type AA , such as chlorine, are considered under the gases. No mixed halogen compound of the type ICl has been studied. Salts of halogen acids, as exemplified by sodium chloride, give rise to no Raman effect because the linkage binding the metallic atom with the hydrogen atom is entirely heteropolar although this statement excludes possible lattice vibrations or shifts $> \Delta\bar{\nu}$ 500. With such an ionic linkage no Raman effect is possible, as there is no actual binding force between the atoms involved.

Polyatomic halogen compounds also may show no Raman lines, as illustrated by magnesium chloride which shows no lines even at a very high concentration. No indisputable Raman shift has been observed for any alkali halide. This is also true of the alkali earth halides with the possible exception of calcium fluoride. Ammonium halides show no Raman shifts other than those lines which may be attributable to the ammonium ion. This ion, like the nitrate ion, is composed of several atoms, and the vibrations between the nitrogen atom and the individual hydrogen atoms may give rise to lines corresponding to the particular group. There is no line corresponding to any vibration between the ammonium ion and the halogen ion.

Between the two extremes of those compounds such as the halides of arsenic, silicon, tin, carbon, antimony, phosphorus, and hydrogen whose linkages are highly homopolar and the heteropolar metallic halides named above, there is a group of compounds which show Raman lines but very weakly. Gold chloride, bismuth chloride, cadmium iodide, and perhaps zinc chloride may be cited as examples of this intermediate type of binding.

The total allowable number of fundamental frequencies which may arise from a compound of the type AX_2 is three. Except in rare cases, however, only one frequency is observed. This means that in the Raman effect this frequency must correspond to the ν_r or ν_1 symmetrical oscillation in a molecule having the symmetry $D_{\infty h}$. In other words the molecule is

symmetrical and linear. The observed shifts for a large number of compounds of this type are indicated in Table 63.

It can be seen from this table that, in a given series, homologous with respect to the halogen present, there is a considerable modification of the ν_1 vibration with different halogen substitution. For example, in liquid mercuric chloride the principal frequency in solution is $\Delta\bar{\nu}$ 320. This drops to $\Delta\bar{\nu}$ 200 in mercuric bromide solution and to $\Delta\bar{\nu}$ 150 in mercuric iodide. Not only is the magnitude of the shift affected by a change in the halogen but, as is to be expected, it is also modified by a change in the cation. The lowest ν_1 type of shift observed in solution is from CdI_2 at $\Delta\bar{\nu}$ 120. The corresponding mercury compound, however, has a shift at $\Delta\bar{\nu}$ 150. Likewise, comparing the cadmium, mercury and zinc chloride with each other, it can be seen that the cadmium compound produces $\Delta\bar{\nu}$ 235, the zinc $\Delta\bar{\nu}$ 275, and the mercury compound $\Delta\bar{\nu}$ 314. It may be seen also that, on occasion, the ν_* type of vibration may be split into more than one component. In mercuric chloride in the crystalline and liquid forms there occur two lines, one at $\Delta\bar{\nu}$ 314 and one 376, the first of which is the much stronger Raman line. As polarization data are lacking it is difficult to account for the appearance of these two lines with any degree of accuracy. One can make the assumption that mercuric chloride may not be entirely linear and that it therefore gives rise to three lines, only two of which have been observed. This explanation, however, is belied by the fact that mercuric chloride solution gives rise to only a single Raman line. Zinc chloride in alcohol solution also exhibits two lines in place of the single line which appears under any other circumstance. Mercurous chloride, however, possesses four Raman lines. This indicates for mercurous chloride the polymerized formula, Hg_2Cl_2 , rather than any formula which might possibly be written as HgCl . Of the four lines recorded, $\Delta\bar{\nu}$ 165 is the strongest and 320 is the weakest. It is probable that $\Delta\bar{\nu}$ 320 represents a harmonic of the line at 165. If this compound was of the type XAAX then three lines should be present, two of which are polarized and one depolarized, the molecule having the symmetry $D_{\infty h}$. No polarization measurement has been made. This is unfortunate because one would be inclined to assign $\Delta\bar{\nu}$ 165 to the vibration where one HgCl group oscillates in a linear symmetrical way against the other HgCl group. Similarly from intensity considerations the $\text{Hg} \leftrightarrow \text{Cl}$ oscillation should take place simultaneously on both ends of the chain and be ascribed to $\Delta\bar{\nu}$ 272, thus leaving as the third frequency the bending type of motion in the molecule. If the other two frequencies are correctly ascribed, then this bending type of motion would remain near $\Delta\bar{\nu}$ 295. However, as a rule, the bending type of motion is of less magnitude than the linear symmetrical type of

oscillation, in consequence of which this shift may represent a combination of ν_4 and ν_6 as observed in acetylene.

Another item of some interest in examining these data in detail is that there is a noticeable diminution in most cases in the ν_1 frequencies in changing from a gas to the liquid, crystalline, or solution states. There is not much alteration in going from the crystalline state to the solution state as compared with the condensation of the gas to a liquid. In this connection Braune and Engelbrecht²⁷⁷ have determined the percentage differences in the frequencies as obtained from the vapor and liquid states of a number of halogen compounds and plotted these against the dipole moments of these compounds. Some of these changes are shown in Table 64 given below:

Table 64.—The Magnitude of the Principal Raman Shifts from Some Halides in the Gaseous and Liquid States

Halide	$\Delta\bar{\nu}$ (gas)	$\Delta\bar{\nu}$ (solution)	$\Delta\bar{\nu}$ (liquid)
HgCl ₂	355	331	314
HgBr ₂	220	205	195
PCl ₃	523		511
AsCl ₃	422		405
SbCl ₃	382		360
AsBr ₃	287		273

The per cent difference between the vapor and liquid spectra of some inorganic halides as a function of the observed moment of these compounds is shown in Figure 57. These authors assume the formation of complex

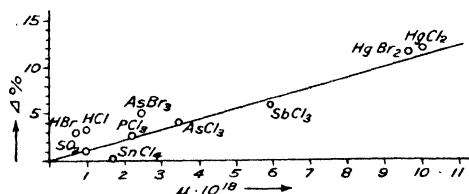


FIGURE 57. The Per Cent Difference between the Vapor and Liquid Phase Raman Spectra of Some Inorganic Halides Plotted against the Observed Moments of these Compounds (after Braune and Engelbrecht).

ions in solution of the type HgCl_4^{--} . In certain cases this has proved to be justifiable but it is not a conclusion which could be reached from the data of Braune and Engelbrecht.

It has been already indicated that there is a change in the magnitude of Raman frequencies depending on the particular anion and cation. This modification, however, is not attributed entirely to a change in mass. There is also a change in force constant. Venkateswaran¹⁶²² has calculated

the force constant for the zinc halides to be 1.6×10^5 dynes cm^{-1} for the chloride and 1.4×10^5 dynes cm^{-1} for the bromide. The values for cadmium chloride, bromide, and iodide in terms of 10^5 dynes cm^{-1} are respectively 1.2, 1.2, and 1.05. The mercuric halides similarly have the following values of the force constant for the chloride, bromide and iodide: 2.3, 1.9, and 1.5. From these data it is evident that the cadmium compounds have the weakest binding force under normal equilibrium displacements. It is likewise noticeable that of all the halogen compounds, the iodide is attached with the weakest binding. This is compatible with the chemical evidence. It should be noted, however, that while, from the point of view of the magnitude of the wave number shifts, the iodine is attached to the cadmium less strongly than chlorine or bromine, the *intensity* of this line, as observed in Raman spectra, is much greater than the intensity of either the chlorine or bromine vibrational lines. This indicates an increase in homopolarity of the molecule in the halide series in going from chlorine to iodine.

Hibben⁷³⁶ has studied in detail the effect of the addition of a chloride ion on the ionization of zinc chloride. Zinc chloride has a Raman shift near $\Delta\bar{\nu}$ 275 which increases in intensity on addition of a chloride ion. It was observed that in concentrated zinc chloride solution the zinc chloride shift attained a considerable intensity, but that on dilution the diminution in intensity of the shift was greater than the diminution in concentration. There is evidently, in solution, an equilibrium between un-ionized ZnCl_2 and Zn^{++} and Cl^- . The equilibrium is shifted in the direction of the production of the zinc ions and chloride ions in the more dilute solutions. If this is the case then the addition of chloride ion to the solution would repress the ionization of zinc chloride and favor the formation of additional molecules of un-ionized zinc chloride. This un-ionized zinc chloride is the only group in the solution which is responsible for the production of the Raman lines. Consequently by this method one can determine the effect of the repression of ionization of the zinc chloride by the addition of common ions. These results are shown in Figure 58. Curve 1 in this figure shows the zinc chloride line as determined in a one-molal zinc chloride solution. Microphotometer tracings also indicate a water band as well as the principal zinc chloride line. In Curve 2 are shown the results obtained with a half-molal zinc chloride solution. Here it is evident that there has been a great diminution in the intensity of the zinc chloride line and this diminution is much greater than the expected one-half, which would be proportional to the dilution. Curves 3, 4, and 5 represent the effect of the addition of sodium chloride to the solution. Here it is noticeable that in the half-molal zinc chloride solution containing two-molal sodium chloride, the intensity of the zinc chloride line is greater than the

intensity of the same line in a one-molal zinc chloride solution containing no sodium chloride.

The effect of the addition of zinc ion to a solution containing zinc chloride was also determined. The zinc ion obtained from zinc sulfate

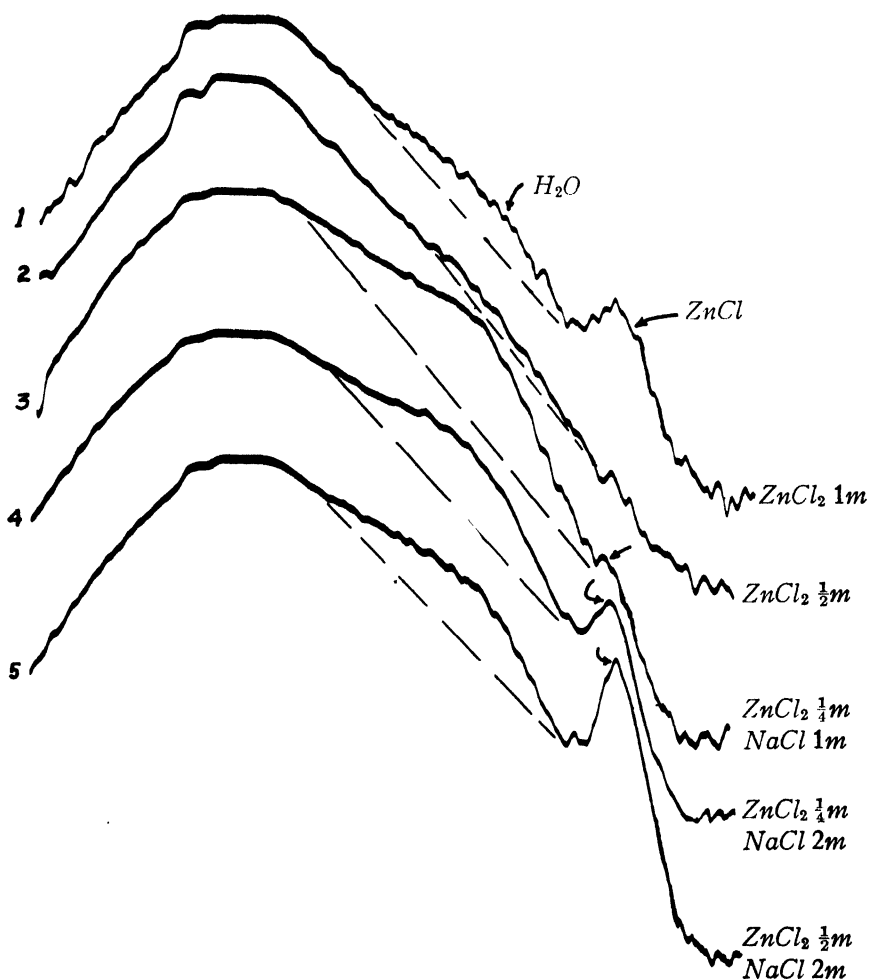


FIGURE 58. A Microphotometer Tracing of Zinc Chloride and Zinc Chloride-Sodium Chloride Raman Spectra showing the Common Ion Effect in Solution.

does not noticeably repress the ionization of zinc chloride but leaves the equilibrium relatively undisturbed. This is due possibly to the equal homopolarity of the bonds in both cases. It was noted also that the addition of sodium chloride to a solution of zinc sulfate resulted in the

formation of the proportional amount of zinc chloride. This raises an interesting question in regard to what happens when potassium bromide is added to a solution of cadmium iodide as reported by Venkateswaran.¹⁶²² It was indicated that the only effect was a strengthening of the cadmium iodide line. In view of the ionic interchange in the zinc solutions, it seems peculiar that there is not produced a Raman shift from cadmium bromide as well as from cadmium iodide as a result of ionic interchange in the cadmium iodide-potassium bromide mixtures in solution. If cadmium bromide were produced two Raman lines should appear in this solution, one near $\Delta\bar{\nu}$ 125 for the cadmium iodide and one near $\Delta\bar{\nu}$ 166 for the cadmium bromide. Only the iodide line has been reported. This interpretation of the results may be different from that intended by Venkateswaran.

Delwaulle, Francois and Wiemann⁴⁷³ have investigated aqueous and alcoholic solutions of zinc and cadmium iodides and have come to the conclusion that zinc iodide may exist as ZnI_2 and as two different complexes, while cadmium iodide exists as CdI_2 and one complex.

For zinc iodide there are three Raman lines in aqueous solution, $\Delta\bar{\nu}$ 106(5), 126(8), and 150(5). In solutions of various alcohols from methanol to butanol, the intensities of $\Delta\bar{\nu}$ 106 and 126 progressively decrease while that of $\Delta\bar{\nu}$ 152 increases, until in butanol only $\Delta\bar{\nu}$ 152 is present. In short, as the ionizing capacity of the solvent decreases, the largest frequency becomes stronger. The addition of iodide ions from alkali iodides increases the intensity of $\Delta\bar{\nu}$ 106 and 126. These frequencies are presumed, therefore, to represent the complexes and $\Delta\bar{\nu}$ 150 to represent un-ionized zinc iodide.

This could be regarded differently. If $\Delta\bar{\nu}$ 106 corresponded to zinc iodide and 150 to a Zn—I ion the same effect would be obtained. This would not be consistent, however, with the persistence of $\Delta\bar{\nu}$ 150 in the alcohol solutions. It is probable, therefore, that zinc iodide behaves differently from zinc chloride and that complexes are actually formed.

The same general behavior is noted^{275, 276, 473} for aqueous and alcoholic solutions of cadmium iodide. Delwaulle, Francois and Wiemann have recently made some very interesting observations on the behavior of this compound. From all alcoholic solutions of CdI_2 —ranging from propanol to decanol—there appear two Raman lines $\Delta\bar{\nu}$ 123(5) and 142(10) ($\rho \approx 0.15$), the latter frequency apparently representing the symmetrical vibration of a molecule of the ABA type having the symmetry $D_{\infty h}$. However, in an aqueous solution containing only CdI_2 , and in alcohol solutions containing an alkali iodide, such as have been mentioned above, there appear four Raman lines whose polarizations are compatible with the tetrahedral symmetry T_d . Therefore, in a medium rich in iodine ions there no longer exists simple cadmium iodide but a more complex unit having the properties

Table 65.—The Raman Shifts from Inorganic Halides of the Type AX₃.

Compounds	Raman Shifts				
	156(7)(6/7)	195(5)(0.6)	274(4)	341(2) 369(6)(6/7)	
AsF ₃ (gas)					
AsCl ₃ (gas)			287(8)		
AsBr ₃ (gas)	129(6)		273(10)		
AsBr ₃ (liquid)	96(6)				382(6)
SbCl ₃ (gas)	146(1)	166(4)		312(4)	
SbCl ₃ (cryst.)	130(8)	160(3)		319(8)	360(3)
SbCl ₃ (liquid)	146(1)	169	242(1)		
BiCl ₃ (cryst.)			288		
BiCl ₃ (HCl sol.)	96(8)(0.5)		242(2)(0.75)		
PF ₃ (gas)					
PF ₃ (liquid)					
PCl ₃ (gas)		190(8)(6/7)			
PCl ₃ (liquid)	116(5)(6/7)	162(4)(0.18)(?)	260(8)(0.32)		380(4)(0.28)
PBr ₃					
BF ₃ (gas)			243		
BCl ₃ (gas)			253(8)(6/7)		
BCl ₃ (liquid)			279		
BBr ₃	151				
AsF ₃ (gas)			649(9)	707(10)	
AsCl ₃	406(8)(0.08)				
AsBr ₃ (gas)					
AsBr ₃ (liquid)					
SbCl ₃ (gas)					
SbCl ₃ (cryst.)					
SbCl ₃ (liquid)					
BiCl ₃ (cryst.)					
BiCl ₃ (HCl sol.)					
PF ₃ (gas)	486(3)		840(1)		
PF ₃ (liquid)	487(3)	531(3)	851(5)		
PCl ₃ (gas)		523(8)			
PCl ₃ (liquid)	488(1)(0.75)	512(10)(0.14)			
PBr ₃			783(3)		
BF ₃ (gas)	471				
BCl ₃ (gas)	471(10)(<0.25)				
BCl ₃ (liquid)					
BBr ₃			743		
				1038(1)	1394(0)
				958	996
				946(3)	989(1)
					846

of CdX_4 . This is discussed more fully in Chapter 28 dealing with complex compounds.

Halides of the Type AX_3

The general behavior of this type of molecule is discussed in some detail under the Raman spectra of gases. Here arsine, phosphine and similarly constituted gases are treated in detail. Most of these molecules are pyramidal, have the symmetry C_{3v} and, therefore, give rise to four Raman frequencies, two of which are polarized and two depolarized and doubly degenerate.

If the high and low parallel vibrations are designated by ν_1 and ν_3 , and the high and low perpendicular vibrations are designated by ν_2 and ν_4 , then $\Delta\nu$ 707 in arsenic trifluoride will correspond to the highly polarized oscillation directed along the lines of the valence bonds. The ν_3 or deformation type of oscillation will then correspond to $\Delta\nu$ 341. This leaves then ν_2 as $\Delta\nu$ 644 and ν_4 as $\Delta\nu$ 274. Similarly in arsenic trichloride the ν_1 , ν_3 , ν_2 , and ν_4 oscillations are respectively $\Delta\nu$ 410, 193, 370, and 159. These results, together with those obtained from the antimony, phosphorus, bismuth, and boron halides are indicated in Table 65.

Yost and Sherborne¹⁷⁵⁰ have calculated the angle between the altitude and the edge of the pyramid, and the bond angle formed by the two halogen atoms and the atom at the apex of the pyramid, for arsenic trifluoride, arsenic trichloride, and phosphorus trichloride. The bond angle turns out to be 97° for arsenic trifluoride, 96° for arsenic trichloride, and 101° for phosphorus trichloride. Most of the figures given in the accompanying table are based on the work of Braune and Engelbrecht,²⁷⁷ Bhagavan-tam,^{123, 125} Cabannes and Rousset,³³⁰ Krishnamurti,⁹⁰⁷ Yost and Anderson,¹⁷⁴⁷ Anderson, Lassettre and Yost⁴⁹ and a number of Soviet workers whose results will be discussed in more detail shortly.

Gupta⁶⁸⁰ has recorded a number of new shifts for arsenic and antimony trichlorides at low temperatures, 31° and -180°C . In general the doubly degenerate frequencies are split into several components. At the higher temperatures the spectrum is thus more simple.

In addition to the data given in the preceding table for arsenic tribromide there may be added¹³⁴⁹ $\Delta\nu$ 220(0) which has heretofore been unobserved.

Brodskii and Sack,^{288, 289} Brodskii, Sack, and Besugli,²⁹⁰ and Sack and Brodskii¹³⁹¹ have investigated the influence of arsenic trichloride on the Raman spectrum of a number of solvents and the influence of the solvents on the Raman spectrum of arsenic trichloride.

If arsenic trichloride is dissolved in methyl or ethyl alcohol the Raman shifts of the alcohol remain unchanged, but the arsenic trichloride fre-

quencies near $\Delta\bar{\nu}$ 372 and 410 are reduced to approximately 349 and 389 in methyl alcohol and 343 and 388 in ethyl alcohol. The other Raman frequencies of the arsenic trichloride remain unchanged. It is concluded that the alcohols do not deform the arsenic trichloride molecule strongly, but do change the elastic binding force of the As—Cl bond. When arsenic trichloride is dissolved in carbon tetrachloride or benzene the Raman effect from the organic solvents remains unchanged, while the Raman lines obtained from the arsenic compound are reduced by an extremely small amount. Ashkinazi, Kurnosova, and Finkel'stein,⁷³ Finkel'stein and Kurnosova,⁵⁶³ and Ashkinazi, Kurnosova, and Finkel'stein⁷² have investigated also the Raman effect of electrolytes such as arsenic trichloride, arsenic tribromide, and antimony trichloride, in non-aqueous solutions. These solutions were investigated not only from the point of view of the effect of the solvents on solutes and the solutes on the solvents, but also from that of the effect of the concentration of the solutes in the solvents. Solutions of arsenic trichloride and arsenic tribromide in benzene or ether furnish no new lines corresponding to a solvent complex. The shifts observed from arsenic trichloride and arsenic tribromide are compatible with those obtained by other investigators. Solutions of antimony trichloride in diethyl ether and in benzene indicate no reactions of any sort with diethyl ether; but in the case of benzene two new frequencies appear, $\Delta\bar{\nu}$ 477 and 1236, which these authors⁷³ postulate indicate the compound $2\text{SbCl}_3 \cdot \text{C}_6\text{H}_6$. Yost and Anderson¹⁷⁴⁷ assign to the vibration frequency of arsenic trichloride the respective types of oscillation designated by ν_1 , ν_2 , ν_3 and ν_4 already outlined above, in contradistinction to assignments made by Brodskii and Sack.²⁸⁸

Briegleb and Lauppe^{280, 281, 282} have studied the complex compounds formed by adding hydrochloric and hydrobromic acids to alcohols and ethers, as well as the complexes between alcohols and tin tetrachloride and possibly aluminum trichloride. Addition of alcohols exerts a pronounced effect on the spectrum of tin tetrachloride. The oxonium compounds are treated in Part II and under the complex inorganic compounds in Chapter 28.

The Raman spectra obtainable from boron trifluoride,^{49, 84} as well as from the chloride and tribromide, have been determined by Anderson, Lassettre and Yost.⁴⁹ For the sake of consistency the oscillation frequencies referred to as being ν_1 to ν_4 will have the same designation as is employed for similar groups, such as the NO_3 or CO_3 ion, having a plane structure with a symmetry D_{3h} , where the two doubly degenerate perpendicular oscillations are referred to as ν_3 and ν_4 and the symmetrical parallel one is designated as ν_1 .

On considering first the spectra obtained from boron trifluoride, it seems

immediately evident that there are two many frequencies for a molecule having the plane triangular structure. Two of the frequencies observed are assigned to a ν_1 type of vibration. These are $\Delta\bar{\nu}$ 783 and 886. In addition there are two other frequencies assigned to a ν_3 type of vibration. These are $\Delta\bar{\nu}$ 1038 and 1105. The $\Delta\bar{\nu}$ 1394 is accounted for on the basis that it is a harmonic corresponding to the oscillation $2\nu_2$. This leaves finally $\Delta\bar{\nu}$ 440 corresponding to the oscillation ν_4 . The strong doublet, $\Delta\bar{\nu}$ 783 and 886, is assigned to a vibrational resonance between ν_1 and $2\nu_4$. It seems probable that the larger of this pair of wave number shifts would be considered ordinarily as a harmonic of $\Delta\bar{\nu}$ 440. The intensity relationship, however, would seem to indicate a Fermi type of accidental degeneracy. The two lines at $\Delta\bar{\nu}$ 1038 and 1105 are much more difficult to explain. The explanation for this multiplicity of lines, which appears not only with boron trifluoride but also in the other boron halides, is based on the presence of another isotope of boron. From this point of view $\Delta\bar{\nu}$ 1038 corresponds to the ν_3 frequency from boron having a mass of eleven and $\Delta\bar{\nu}$ 1105 from the boron trifluoride containing boron with mass ten. In boron trichloride the shift $\Delta\bar{\nu}$ 924 represents a harmonic corresponding to $2\nu_2$, but the lines which appear at $\Delta\bar{\nu}$ 958 and 996 are the ν_3 oscillations for boron, with boron isotope eleven and boron isotope ten respectively. From these data the authors have been able to calculate the force constant and internuclear separation of the respective atoms in the molecules. It is noticeable that there is a considerable diminution in the B—Br linkage as compared with the B—F one.

Bailey, Hale and Thompson⁸⁴ do not agree with all of the above data or interpretations as far as boron trifluoride is concerned. They observe $\Delta\bar{\nu}$ 886 for ν_1 , and $\Delta\bar{\nu}$ 440 for ν_4 . However, from infrared experiments there is found the pair of lines $\Delta\bar{\nu}$ 1448, 1501 for ν_3 , and for ν_2 the pair 694, 722. At the same time $\Delta\bar{\nu}$ 862 is attributed to $2\nu_4$ and 1394 to $2\nu_2$. It is not believed that any resonance splitting gives rise to the $\Delta\bar{\nu}$ 783 and 886 mentioned previously,⁴² particularly as no such effect is observed in boron trichloride from the frequencies ν_1 ($\Delta\bar{\nu}$ 471) and $2\nu_4$ ($\Delta\bar{\nu}$ 486). Isotopic structure is observed only in the ν_2 and ν_3 types of oscillation, the last type being observable only in the infrared. These results obtained by different methods cannot be very well reconciled.

Venkateswaran¹⁶¹⁶ has obtained $\Delta\bar{\nu}$ 255(6), 472(10) and 947(0) for boron trichloride. Of these shifts $\Delta\bar{\nu}$ 255 is questionable.

The spectrum of bismuth trichloride in crystalline form has been obtained by Krishnamurti.⁹⁰⁷ On account of the hydrolysis of this compound in solution it has not been possible to examine aqueous solutions of bismuth trichloride without adding hydrochloric acid to prevent hydrolysis. Hydrochloric acid solutions of bismuth trichloride differ appreciably from

the crystalline compounds. This difference rests primarily in the lowest frequency shift which occurs at $\Delta\bar{\nu}$ 96 in the acid solutions and at 146 in the crystals. From the polarization measurements of Bhagavantam^{123, 125} the ν_1 type of oscillation is represented by the frequency occurring at $\Delta\bar{\nu}$ 288. The intensity of the lines from bismuth trichloride are relatively weaker than those obtained with similarly constituted compounds.

The halides of antimony and phosphorus show no particular peculiarities; they have the same configuration and present the same problems as do the arsenic halides. The four expected Raman frequencies are present. According to Yost and Anderson¹⁷⁴⁶ the valence angle in the fluoride and chloride of phosphorus is approximately 100° . This is approximately the value found in the arsenic halides and in phosphine itself. Some of these shifts are also recorded in the table in the section on gaseous compounds.

Halides of the Types AX_4 and ABX_3

The first of these compounds are of the same type as those encountered in the structure of the sulfate ions, the perchlorate ions and carbon tetrachloride. These represent a tetrahedral structure having the symmetry T_d and consequently give rise to four Raman frequencies, one of which is polarized. The remaining three are depolarized, two of them are triply degenerate and one doubly degenerate. In this model the cation is considered as being in the center of the tetrahedron. The ν_1 symmetrical type of vibration therefore is supposed to be the symmetrical expansion and contraction of the tetrahedron, that is, the movement of the four atoms in a direction away from or toward the central atom. In all three of the other vibrations the central atom takes a prominent part. In one type, for example, the atom at the apex of the tetrahedron and the central atom may vibrate in unison toward the base of the tetrahedron while, at the same time, the other atoms are vibrating in a direction nearly perpendicular to the base. In another mode of oscillation the atom at the apex and the central atom are vibrating toward and away from each other and, at the same time, the other three atoms are vibrating in a general direction toward and away from this pair of atoms. The fourth type of motion occurs when the atoms at the bottom of the tetrahedron and the one at the apex are vibrating asymmetrically in relation to each other and in relation to the central atom. While polarization measurements suffice to distinguish the symmetrical vibration which is polarized from the other vibrations, it is difficult from a Raman spectrum point of view to ascertain what numerical frequencies correspond to each of the three triply and doubly degenerate vibrations.

The compounds in this group consist primarily of the halogen derivatives of silicon, tin, titanium, and germanium. The silicon derivatives will

Table 66.—The Raman Shifts from Some Inorganic Halides of the Type AX₄.

Compounds	Raman Shifts				
SiF ₄ (incomplete)					
SiCl ₄					221(5) (6/7)*
SiBr ₄	90(3)				
SnCl ₄ (gas)					
SnCl ₄	107(5) (6/7)	130(6) (6/7)			
SnBr ₄	88(3)				220(4)
SnBr ₄ (combina-					
tions)					
TiCl ₄		128	144	176	193
GeCl ₄		120(3) (6/7)	145(0) (6/7)		
GeBr ₄	78	132(6)	171(7)		234
SiF ₄ (incomplete)					
SiCl ₄					800(10)
SiBr ₄	249(4)				
SnCl ₄ (gas)					
SnCl ₄	366	400			
SnBr ₄	367(8) (0.05)	403(2) (6/7)			
SnBr ₄ (combina-					
tions)					
TiCl ₄	305	370	438	497	
GeCl ₄		382(6) (0.14)		494(0) (6/7)	
GeBr ₄		397(10)		451(1)	
		328			

* The second number given in parentheses indicates degree of polarization.

be treated in more detail under silicon compounds as far as their relationship to other silicon compounds is concerned. Raman shifts of all these compounds are given in Table 66. These results are mainly based on the work of Bhagavantam,^{123, 125, 126, 148} Cabannes and Rousset,^{328, 329, 330} Trumpy,^{1583, 1585} Braune and Englebrecht,²⁷⁷ and Landsberg and Malyshev.⁹³⁹

It is apparent from the table that as far as the symmetrical valence vibration is concerned, the binding force between the cations and halogen atoms in these compounds decreases in the order silicon, germanium, titanium and tin. In every case there are the four expected Raman frequencies, each of which has approximately the correct depolarization factor. With silicon tetrachloride there is an additional vibration at $\Delta\bar{\nu}$ 440 which, according to Ananthakrishnan,²² is a harmonic of $\Delta\bar{\nu}$ 221. The depolarization measurements are sufficiently accurate to indicate which is the ν_1 type of vibration. The actual numerical values of these depolarization measurements for these compounds should, however, be accepted with the proverbial "grain of salt." Various observers differ by nearly 100 per cent.

Considerable difficulty is encountered in determining the Raman spectra of certain of these halides. Thus Gueron⁶⁷⁰ has pointed out the difficulties in the determination of the Raman spectrum of tin tetrachloride solutions due to hydrolysis. His results indicate the possibility of the existence of a complex ion SnCl_6 . Landsberg and Malyshev⁹³⁹ have observed a number of Raman frequencies for tin tetrabromide according to the following scheme:

Fundamentals	Combinations
A = $64(\nu_2)$	2A, 2B, 2C
B = $88(\nu_4)$	B + D, B + C, D - B, C + D
C = $220(\nu_1)$	
D = $279(\nu_3)$	

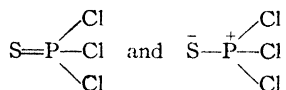
The second order rays observed by these authors have a ratio of approximately one tenth of one per cent of the fundamental intensity.

Yost, Lassettre and Gross¹⁷⁴⁹ have observed $\Delta\bar{\nu}$ 800 for silicon tetrafluoride. At the same time, from theoretical considerations, they postulate the other three frequencies for silicon tetrafluoride as being $\Delta\bar{\nu}$ 285, 1000 and 431. Ananthakrishnan²² has suggested that the broadening of the fourth frequency in the case of silicon tetrachloride may be due to a cause similar to that which brings about the splitting of the fourth frequency in the case of carbon tetrachloride. Mention should be made of the observation of Haun and Harkins⁷⁰³ on the spectrum of germanium tetrachloride. These observers have obtained four frequencies, of which $\Delta\bar{\nu}$ 397 and 132 correspond to optically inactive vibrations which do not

affect the electric moment (ν_1 and ν_2); while ν_3 and ν_4 , corresponding to $\Delta\bar{\nu}$ 451 and 171, are the optically active frequencies.

Tchakirian and Volkringer¹⁵³⁴ have recorded for germanium tetrabromide the wave number shifts $\Delta\bar{\nu}$ 78, 111, 234 and 328. It is noticeable in comparing the frequency shifts observed from all of these compounds that the largest frequency shift is the one most sensitive to changes in mass of the cation. This is the ν_3 antisymmetrical vibration.

Two other halides, phosphorus oxychloride and phosphoryl chloride, should also be mentioned. Venkateswaran¹⁶¹⁶ and Thatte¹⁵⁴¹ obtained from phosphorus oxychloride $\Delta\bar{\nu}$ 191(4), 269(2), 388(4), 485(6), 585(0), and 1290(1), and Thatte¹⁵⁴¹ obtained from thiophosphoryl chloride (or phosphorus thiochloride) $\Delta\bar{\nu}$ 171, 246, 382, 432, 543, 750. These are in reasonable agreement with the results of Simon and Schulze.¹⁴⁴² All the lines observed in phosphorus trichloride with the exception of $\Delta\bar{\nu}$ 514 are found in the oxychloride. In addition there is a new frequency at $\Delta\bar{\nu}$ 1290 which is attributed to the presence of a P=O group. Thatte assumes that the spectrum from thiophosphoryl chloride should be similar to that observed from the oxychloride if both have an asymmetric tetrahedral structure of symmetry C_{3v} , which should yield six Raman lines. There does seem to be a general similarity between these two compounds. The slight reduction in value of the Raman shift in thiophosphoryl chloride is presumably due to the substitution of the oxygen atom in the oxychloride by an atom of sulfur. Just as the shift at $\Delta\bar{\nu}$ 1290 has been assigned to a $C \leftrightarrow O$ oscillation in the oxychloride, the similar shift at $\Delta\bar{\nu}$ 750 in thiophosphoryl chloride can then be assigned to the P=S bond. Of the structures proposed for this compound



the second seems the more likely.

Gopala Pai⁶²³ has studied the Raman effect from phosphonium iodide with the view of correlating it with the crystalline structure of the compound. All the observed frequencies, namely, $\Delta\bar{\nu}$ 930, 1040, 1130, 1259, 1416, 2304, and 2370, were attributed to the phosphonium ion $[\text{PH}_4]^+$.

Silicon compounds of the type ABX_3 are dealt with in Chapter 26.

Halides of the Types AX_5 and AX_6

Phosphorus pentachloride⁹⁰⁷ and antimony pentachloride¹³⁴⁸ are the only compounds having the configuration AX_6 which have been studied. In both these cases the spectra are evidently incomplete. It is supposed that phosphorus pentachloride has the symmetry D_{3h} , and antimony

pentachloride the symmetry C_{4v} . Few of the lines in phosphorus pentachloride correspond to those observed from phosphorus trichloride.

Moureu, Magat and Wetroff¹¹⁴¹ (Raman Jubilee volume) agree substantially with Krishnamurti⁷³⁶ so far as solid phosphorus pentachloride is concerned. This compound is presumed to have the regular tetrahedral structure containing a PCl_4 -group with the other chlorine attached by a *quasi* electrovalent binding which may be indicated by $PCl_4^+ Cl^-$. Polarization measurements would be of value in substantiating this hypothesis.

The liquid, however, gives a greatly altered spectrum. The compound is supposed to have a ditrigonal pyramidal structure, the chlorine atoms being identical and bound to the phosphorus by homopolar bonds.

Redlich, Kurz and Stricks¹³⁵⁰ add two lines to the spectrum of anti-mony pentachloride previously observed, namely $\Delta\bar{\nu}$ 165(2) and 581(1). Moureu and co-workers (Raman Jubilee volume) have obtained from niobium pentachloride $\Delta\bar{\nu}$ 170, 356, 400, 427, and from tantalum pentachloride 115, 175 and 413. These are incomplete results.

In the AX_6 group are considered substances such as sulfur hexafluoride, chlorotitanic acid and other similar compounds. Some of these have been casually treated elsewhere.

In investigations of the Raman spectrum of titanium tetrachloride Rumpf¹³⁹⁰ has observed, in addition to the lines ascribed to titanium tetrachloride, three lines which are extremely feeble and occur near $\Delta\bar{\nu}$ 631, 785, and 926. These are attributed to a molecular association and disappear with the elevation of temperature. In solutions containing titanium tetrachloride these are absent and three new lines appear. These are $\Delta\bar{\nu}$ 251, 340 and 463, of which the first two lie between the first and second pair of lines reported in Table 66. The intermediate frequency is broad and seems to be a doublet. This is similar to the observations which have been made with H_2SnCl_6 which equally possesses the Raman lines in the position intermediate between the two groups of two lines of stannic chloride and in which the intermediate frequency is also particularly broad and seems to be a doublet. The addition of a small quantity of water to the hydrochloric-acid solution of titanium tetrachloride causes the disappearance of any lines attributable to H_2TiCl_6 .

The work of Gueron⁶⁷⁰ has been referred to briefly. Solutions of stannic chloride possess no Raman lines which correspond to the liquid but agree with the lines of the ion $SnCl_6$. The Raman spectrum of a saturated solution of the compound $SnCl_4 \cdot 5H_2O$ at ordinary temperatures shows the same spectrum. According to the author, this does not preclude the existence of complexes other than $SnCl_6$. Furthermore, with dilution, the lines which correspond to this complex ion persist even after the

beginning of the formation of a strong Tyndall effect. The hypothesis is advanced that the ion SnCl_6 dissociates into Sn^{++++} and Cl^- . The tin ions are transformed by the action of water into $\text{SnO}_2 \cdot x\text{H}_2\text{O}$.

Redlich, Kurz, and Rosenfeld¹³⁴⁸ report results obtained from HSbCl_6 which yielded $\Delta\bar{\nu}$ 172(5), 277(4), 337(7), 419(1), and possibly 605(0). The compounds H_2SnCl_6 , Li_2SnCl_6 and MgSnCl_6 yield on the average $\Delta\bar{\nu}$ 158(3), 235(3), and 316(5), from which it is precariously concluded that the shifts observed for the SnCl_6 ion are $\Delta\bar{\nu}$ 156(4), 235(3), and 341(7). These shifts, as others in this particular type of grouping, are not included in tabular form because of their uncertainty.

Subsequently Redlich, Kurz and Stricks^{1350,1351} have observed from H_2SnBr_6 $\Delta\bar{\nu}$ 71, 102, 142, 183, 208; from MgSnBr_6 $\Delta\bar{\nu}$ 69, 144 and 183 (incomplete); and from H_2SeCl_6 $\Delta\bar{\nu}$ 166(1), 273(2), 346(3). The symmetry of the ion SnBr_6 is apparently less than octahedral and the existence of H_2SeCl_6 may be inferred from the spectrum of SeCl_4 dissolved in hydrochloric acid. The molecular frequencies of these compounds are deduced by means of Placzek's selection rules, and Bjerrum's central force principle. For compounds of the type AX_6 the results do not agree with those obtained by applying the valence force principle. Of the more complicated compounds of the type SF_6 studied by Yost, Steffens, and Gross,¹⁷⁵¹ there apparently are three typical frequencies, $\Delta\bar{\nu}$ 522(1), 642(1), and 775(10). These are within reasonable agreement with the results of

Table 67.—The Raman Shifts from Some Inorganic Halides of the Type AX_6 and AX_6 .

Compounds	Raman Shifts				
SF_6 (liquid)					
SeF_6 (liquid)					
TeF_6 (liquid)					316(4)
SbCl_5 (liquid)		165(2)	178(6)		304(4)
PCl_5 (cryst.)				248(1)	
PCl_5 (liquid)	100(10)(P)		190(1)(6/7)	271(6)(6/7)	
SF_6 (liquid)			522(2)	642(2)	776(10)
SeF_6 (liquid)	405(2)			662(0)	710(10)
TeF_6 (liquid)				672(0)	697(10)
SbCl_5 (liquid)	355(7)	399(4)		538(1)	
PCl_5 (cryst.)	356(4)	404(0)	449(1)		
PCl_5 (liquid)		392(6)(P)	449(0)(6/7)	495(0)(6/7)	

Epstein and Steiner⁵³⁵ and Eucken and Ahrens⁵³⁷ as far as the application to sulfur hexafluoride is concerned. From the point of view of infrared absorption in relation to sulfur hexafluoride⁵³⁷ this absorption corresponds to $\Delta\bar{\nu}$ 363, 525, 617, 645, 775, 965.

Redlich, Kurz and Rosenfeld¹³⁴⁹ state that there is no essential difference

between their interpretation of the SF_6 assignments and that given by Yost, Steffens and Gross.

Sulfur hexafluoride is an octahedral molecule and should give rise to three Raman frequencies, two of which are depolarized and one polarized. The depolarized frequencies are doubly and triply degenerate. Of these three observed Raman shifts, the one corresponding to ν_1 is the largest. If the lowest frequency shift is assigned to the ν_3 deformation vibration the relation $\nu_1^2 = \nu_2^2 + (3/2) \nu_3^2$ is found to hold.

Selenium hexafluoride and tellurium hexafluoride¹⁷⁵¹ have somewhat similar spectra. For the former of these two compounds are found $\Delta\bar{\nu}$ 405(2), 662(2), 710(10) and for the latter $\Delta\bar{\nu}$ 316(4), 672(2) and 697(10). These results are shown in Table 67.

Yost (Raman Jubilee volume) has recently made an analysis of the spectra obtained from the volatile fluorides including thionyl fluoride.

Chapter 24

The Raman Effect in Acids

One of the fruitful applications of the Raman effect is in the investigation of the constitution of acid solutions of varying concentrations. While conductivity measurements and determinations of hydrogen-ion concentrations by various methods have given a picture of the step-wise dissociation of polybasic acids as well as of the fraction of undissociated molecules remaining in solution, practically no such method has any meaning in solutions of high concentration. The Raman method, on the contrary, can be applied to pure liquid acids as well as to aqueous solutions of acids. Not only is it possible to follow a normal dissociation phenomenon, but it is also possible to distinguish and identify the appearance of other molecular species which may be coexistent. This information is obtained in the following way. In an experiment, if the time of exposure is increased in proportion to dilution, the intensity of the Raman lines characteristic of the substance examined will remain constant provided no other factor intervenes. If, however, dilution or concentration under these conditions causes a change in the molecular configuration or constitution of the acid, a corresponding anomalous Raman effect will result. As will be seen later, the constitution of a number of acids has been determined by this method.

Diatomic Halogen Acids

It is possible to determine the spectra of hydrogen chloride, bromide and iodide in the gas phase. Under these conditions the H—X linkage is homopolar and will give rise to a Raman line corresponding to the simple oscillation of the hydrogen atom against the halogen atom. The question may be properly raised whether, under these conditions, these compounds are acids, but this question is of no concern at the moment. It might be more proper to discuss these compounds under gases but, as has been stated in the introduction, when a compound may be properly considered in more than one category, it will be discussed with that group with which it is most closely allied. For this reason the halogen acids are dealt with here. They were mentioned, however, in chapter 20.

The actual magnitude of the H—X shift depends greatly upon the state of aggregation. The effect of a change of state is more pronounced in the case of these acids than it is with almost any other compound. The

principal shifts for hydrochloric acid are $\Delta\bar{\nu}$ 2880(5) (gas), $\Delta\bar{\nu}$ 2778(5) (liquid), $\Delta\bar{\nu}$ 2760(5) (solid), although Lee, Sutherland and Wu report two lines for crystalline hydrogen chloride $\Delta\bar{\nu}$ 2709(8) and 2759(4). For hydrobromic acid the shifts are $\Delta\bar{\nu}$ 2558(3) (gas), $\Delta\bar{\nu}$ 2487(3) (liquid), $\Delta\bar{\nu}$ 2465(3) (solid) and for hydriodic acid, $\Delta\bar{\nu}$ 2233(2) (gas), $\Delta\bar{\nu}$ 2165(2) (liquid) and $\Delta\bar{\nu}$ 2160(2) (solid). In addition to the decrease in the frequency shifts as a result of a change in state there is also marked diminution in going from a lighter halogen to a heavier one. This is to be expected from the point of view of the mass effect and is fairly nearly proportional to the increased mass involved. All these lines are rather broad and probably are made up of more than one component. It has been pointed out by Callihan and Salant³⁸² that the decrease in the frequencies as a result of changes in state cannot be accounted for on the basis of Lorentz-Lorenz forces.

In aqueous solutions of hydrochloric acid there are no lines observed attributable to hydrogen chloride but there is a decrease in the width of the water band in the more concentrated solutions. These results are to be expected if hydrogen chloride is completely ionized in solution.^{48, 344, 594} Woodward^{1729, 1731} investigated the Raman spectrum of hydrochloric acid in the organic solvents benzene, xylene and carbon tetrachloride, but could find no evidence of any associated hydrochloric acid. West and

Table 68.—The Raman Shifts from Hydrochloric and Hydrobromic Acids in Various Solvents.

Solvent	Dielectric Constant	HCl Solutions $\Delta\bar{\nu}$
HCl gas		2886
SiCl ₄	2.5 calc.	2860
PCl ₃	4.2	2828
CHCl ₃	7.0	2826
HCl liquid	8.85(– 90° C.)	2800
SO ₂	22.4	2798
C ₂ H ₅ Br	14	2797
CH ₃ CO·Cl	20.3	2804
		HBr Solutions $\Delta\bar{\nu}$
HBr gas		2559
CHCl ₃	7.0	2500
HBr liquid	6.29(– 80° C.)	2487
C ₂ H ₅ Br	14	2471

Arthur¹⁶⁷⁹ more recently examined solutions of hydrochloric and hydrobromic acids in non-ionizing solvents. By working at a low temperature, solutions were prepared of sufficient concentration to show the Raman line of the solute. The conclusion is reached that there is a definite relation between the relative frequency displacement and the dielectric constant of the solvents for the dissolved molecules of HCl and HBr. On the

other hand, concentrated solutions of hydrogen chloride and hydrogen bromide in ionizing solvents show no features which can be identified as H—X vibrations. The alteration in the H—Cl and H—Br Raman lines as a function of the dielectric constant or change in solvent is indicated in Table 68.

In interpreting the frequency changes of these acids it is necessary first to ascertain if hydrochloric acid is polymerized at all. At least in the liquid form this does not seem to be the case. Its Trouton constant and Eötvös constant are both normal. One is led to the conclusion that the diminution in the vibrational frequency therefore points to a diminution in the force constant. In this case, as West and Arthur indicate, if the empirical rule of Morse ($\nu^3 = \text{constant}$) is applicable, the internuclear distance at equilibrium must also increase. It is also interesting to note that there is a maximum value which can be attained in the direction of the diminution of the attractive force. This value is approximately six per cent of the force prevailing in the isolated molecules. No process of dissociation, therefore, of hydrochloric acid or hydrobromic acid can take place purely by electrostatic action. Dissociation occurs only where there is an atom capable of combining with a proton.

Woodward also investigated the Raman spectrum of hydrofluoric acid (40-per cent). It is well known that this acid is polymerized in the vapor phase, and conductivity measurements would indicate the presence of an HF_2 ion from the dissociation of H_2F_2 .^{71, 465} No Raman lines were observed. However, a strong continuous background spectrum is present which tends to mask any weak Raman lines. The lack of positive results, in spite of the experimental difficulty mentioned, is surprising if hydrofluoric acid has the constitution generally attributed to it. It is probable that this material will be reinvestigated and this point clarified.

Sulfuric Acid

Sulfuric acid is an interesting example of the investigation by means of the Raman effect of the constitution of a substance not amenable to study by other methods. This acid exhibits many anomalies in its spectra which can be explained only on the basis of a profound modification of its constitution as a function of concentration. Sulfuric acid was investigated early in a qualitative fashion by a number of workers.^{118, 594, 1412, 1532, 1660} Nisi¹¹⁷⁶ observed that the spectrum of the pure acid was quite different from that of a dilute solution. Bell and Frederickson,¹¹³ Fadda⁵⁴⁰ and Specchia¹⁴⁹⁷ noted the appearance and disappearance of some lines depending on the concentration of the acid. Woodward^{1729, 1731} and Woodward and Horner¹⁷³³ investigated the spectra obtained from the acid in various concentrations. These results are indicated in Figure 59. Here it is

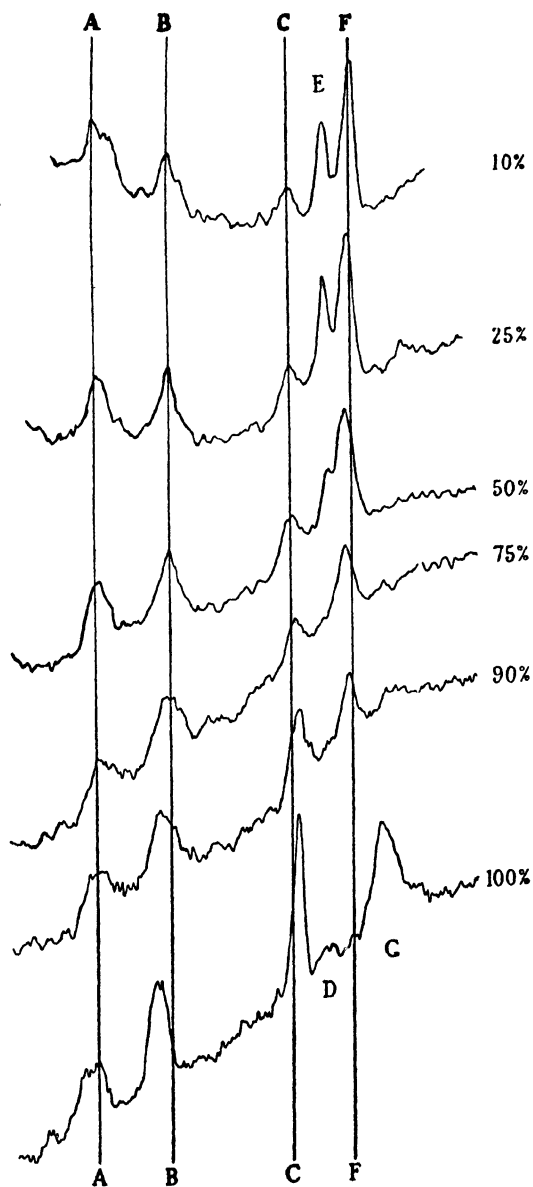


FIGURE 59. The Raman Spectra of Sulfuric Acid at Different Concentrations (after Woodward and Horner).

shown quite clearly that there is a pronounced change in the spectra with increasing concentration. The significance of these changes will be dealt with shortly.

There is not only a change of intensity and an appearance of new lines at different concentrations, but also a possible shifting of the maxima of some of those lines which persist through a wide concentration range. The exact interpretation of this behavior is subject to some difference of opinion. Bell and Jeppesen¹¹⁵ have determined the Raman spectra of sulfuric acid from 10 to 100 per cent in steps of 5 per cent with the results indicated in Figure 60. In the 100 per cent solution line 1 and line 4'

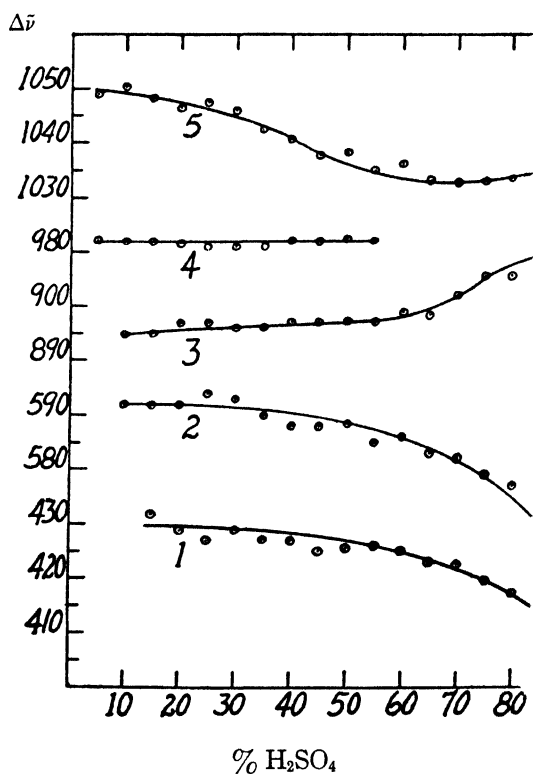


FIGURE 60. The Change in the Principal Raman Shifts from Sulfuric Acid (after Bell and Jeppesen). Corrected to data.

(not shown in the figure) at $\Delta\bar{\nu}$ 972 are probably masked by the strong continuous background. According to these authors the line at $\Delta\bar{\nu}$ 972 is not to be confused with $\Delta\bar{\nu}$ 982 which begins to appear in a sulfuric acid solution of 55 per cent. The interpretation made of these results is that

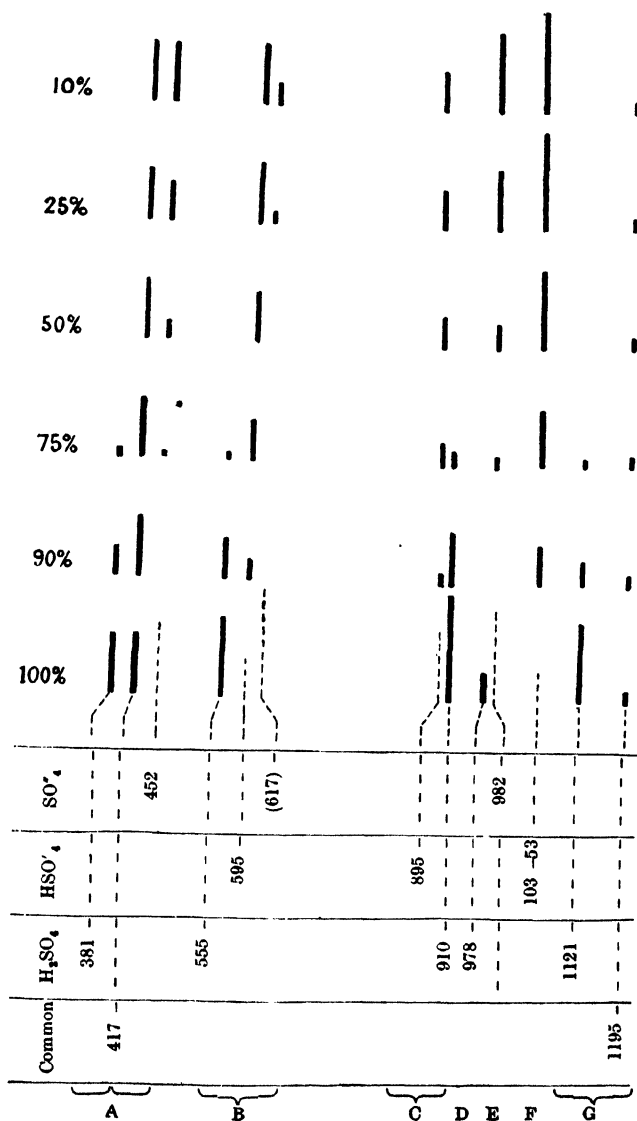


FIGURE 61. The Distribution of Raman Shifts from Sulfuric Acid at Varying Concentrations (after Woodward and Horner).

there is a gradual increase in frequency of $\Delta\bar{\nu}$ 409 with dilution. The Raman frequency at $\Delta\bar{\nu}$ 562 shows a similar increase on dilution. However, there is presumed to be a decrease in the frequency of $\Delta\bar{\nu}$ 911 with dilution until an approximate 65-per cent concentration of the acid is reached, following which the value remains relatively constant. The $\Delta\bar{\nu}$ 980 which appears at 55 per cent remains practically at the same value to 5 per cent. On the other hand, $\Delta\bar{\nu}$ 1038 at first decreases gradually to $\Delta\bar{\nu}$ 1034 and then increases to $\Delta\bar{\nu}$ 1049.

It is argued that this behavior is real and that the shift of the maximum cannot be ascribed to a variation in intensity of several possible components comprising each line, as there would be some concentration which would be favorable to the simultaneous appearance of the two or more components. It is also pointed out that $\Delta\bar{\nu}$ 1151 and 1352 are in the approximate positions of the strongest lines for sulfur dioxide observed by Bhagavantam.¹²⁵

Woodward and Horner¹⁷³³ have quantitatively studied the spectra of sulfuric acid at six different concentrations. In general, the observations of Bell and Jeppesen are in fair agreement with those of Woodward and Horner. In the more concentrated acid solutions, however, the latter authors record $\Delta\bar{\nu}$ 381, 417, 452, 555, 595, 617, 895, 910, 978, 982, 1036, 1121, 1195. Of these, the first three tend to merge into one line, the second three into another, the next two into a third, and the last two into a fourth. The $\Delta\bar{\nu}$ 978, 982 and 1036 remain as separate lines. The variation in intensity of these components would produce an apparent shift of the maxima of the somewhat broad lines recorded photographically.

The mechanism by which Woodward and Horner account for the shifts in the maxima and the changes in intensity with dilution is indicated in Figure 61. It is to be emphasized that the exact frequencies which would give rise to this shifting of the maxima were not observed in all cases by the authors. However, Chédin³⁶⁰ records a doublet for the first line in 100-per cent sulfuric acid, namely, $\Delta\bar{\nu}$ 395(8) and 480(8) (cf. Woodward and Horner $\Delta\bar{\nu}$ 381, 417, 452, Catalan and Yzu³⁴⁹ $\Delta\bar{\nu}$ 388, 416, and Médard¹⁰⁶⁴ $\Delta\bar{\nu}$ 391 and 433). For the second group of lines Chédin observes 560(7), Bell and Jeppesen $\Delta\bar{\nu}$ 561(4), Catalan and Yzu $\Delta\bar{\nu}$ 554, 586, 644, and 742, and Woodward and Horner $\Delta\bar{\nu}$ 555, 595, and 617. For the third group^{349, 1733} there are $\Delta\bar{\nu}$ 895 and 910, there being no doubt about $\Delta\bar{\nu}$ 910.^{115, 349, 360, 1733} The appearance of $\Delta\bar{\nu}$ 1121 and 1195¹⁷³³ is partially confirmed by $\Delta\bar{\nu}$ 1131 and 1174³⁴⁹ observed independently. Finally $\Delta\bar{\nu}$ 1370, 1359, or 1352 (representing but one actual line)^{349, 360, 779} apparently are real. These results are summarized in Figure 62 which shows the results obtained by a number of investigators for the concentrated acid.

Attention is likewise called to the fact that Médard and Marchand¹⁰⁷⁴

have observed $\Delta\bar{\nu}$ 404, 591, 1191, and 1395 for the sulfate group in diethyl and dimethyl sulfate. These are the values extracted from the complete

spectra for both these compounds and presumably refer to the $\begin{array}{c} \bar{O} \\ \diagup \\ S \\ \diagdown \\ \bar{O} \end{array}$ portion of the molecule. There is a line which occurs at $\Delta\bar{\nu}$ 422 in diethyl sulfone which is at least partially analogous to the doublet 391–433 of sulfuric acid. In contradistinction to this, in the dimethyl and diethyl sulfates there is no analogous shift corresponding to $\Delta\bar{\nu}$ 910 and 745. These authors conclude that pure sulfuric acid possesses a molecular structure which is strongly deformed in comparison with its alkyl derivatives.

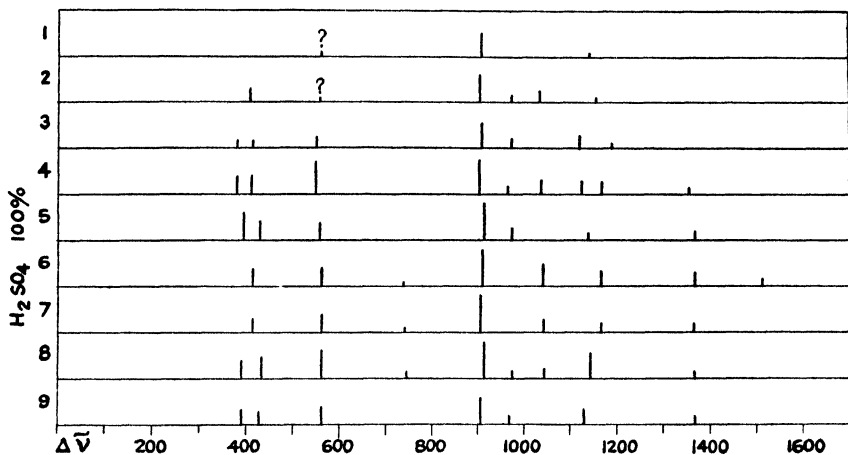


FIGURE 62. The Raman Spectra of Pure Sulfuric Acid according to Different Observers.

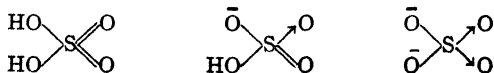
It has been pointed out by I. R. Rao,¹³⁰⁹ Woodward and Horner, and others that the frequencies at approximately $\Delta\bar{\nu}$ 910, 978, 1121, and 1360 which are characteristic of the H_2SO_4 molecule and are present in the spectrum of the pure acid, either vanish rapidly or decrease in intensity on dilution. On the other hand the frequency $\Delta\bar{\nu}$ 1038, which occurs in the concentrated acid and is presumably characteristic of the $[HSO_4]^-$ ion, increases in intensity. The frequency $\Delta\bar{\nu}$ 982, which appears at nearly 50 per cent acid and is presumably characteristic of the sulfate ion, becomes stronger with dilution. Based on this view the characteristic frequencies for H_2SO_4 are $\Delta\bar{\nu}$ 381, 555, 910, 978, and 1121; for $[HSO_4]^-$ $\Delta\bar{\nu}$ 595, 895, and 1036; $[SO_4]^{--}$ 452, 617, and 982; while 417 and 1195 are common to all.

The exact assignment of some of these frequencies to specific ionic or molecular configurations varies with different authors. Notwithstand-

ing this difference of opinion, in general it can be stated that $\Delta\bar{\nu}$ 389, 553-910, 970, 1131 and 1360 diminish markedly in intensity with dilution of the pure acid to a concentration of approximately 75 per cent, at which point they become practically extinct. Perhaps, among these shifts, $\Delta\bar{\nu}$ 553 and 910 are shifted to $\Delta\bar{\nu}$ 595 and 895. On the contrary, $\Delta\bar{\nu}$ 1038 increases quite markedly in its intensity with dilution, as does also $\Delta\bar{\nu}$ 982. The latter shift is not to be confused with $\Delta\bar{\nu}$ 970 already referred to. These shifts at $\Delta\bar{\nu}$ 553 and 910 are apparently replaced at 90 per cent concentration by two others, $\Delta\bar{\nu}$ 586 and 898 respectively. As pointed out previously, there is a difference of opinion as to the genuineness of the replacement rather than a change in the maximum. There is some evidence in solutions of 75 per cent for the appearance of a shift at $\Delta\bar{\nu}$ 448 which increases in intensity with dilution. At the same time $\Delta\bar{\nu}$ 416 appears in all dilutions and remains at constant intensity. The latter two lines have been frequently considered as a singlet rather than a doublet with a maximum at $\Delta\bar{\nu}$ 433.

The explanation of this general behavior has already been indicated. The extremely concentrated solution contains lines which are due to molecular sulfuric acid. The first step in the dissociation process of the solution is the production of HSO_4 ions. This is characterized by $\Delta\bar{\nu}$ 1038. This frequency is completely absent in the spectrum of pure sulfuric acid if extreme care is employed to avoid any contamination with water. The production of HSO_4 ions consequently reduces the concentration of unionized homopolar sulfuric acid, with a resulting diminution of the intensity of $\Delta\bar{\nu}$ 910 characteristic of this acid. The second stage in the ionization process is the complete ionization of the acid to sulfate ion and hydrogen ion. This is characterized by the appearance of $\Delta\bar{\nu}$ 982 at approximately 50 per cent acid and the increase in intensity of this frequency shift with dilution. The frequencies which persist in dilution near $\Delta\bar{\nu}$ 430 and 600 are also present in sulfate ions whose origin is one of the alkali sulfates.

The polarization measurements of Venkateswaran¹⁸³¹ on 99-per cent and 25-per cent sulfuric acid indicate that $\Delta\bar{\nu}$ 896, 982, and 1024 are nearly equally polarized ($\rho = 0.17, 0.03$, and 0.24 respectively) in the 25-per cent solution, while those below $\Delta\bar{\nu}$ 593 are depolarized in both the concentrated and the dilute acid solutions. In the 99-per cent solution $\Delta\bar{\nu}$ 910 has a value for ρ of 0.16. Consequently this frequency probably corresponds to the symmetrical expansion and contraction of the tetrahedron. The structures existing during the ionization process of sulfuric acid are presumed by Venkateswaran to be



Of these, the middle form corresponding to $[\text{HSO}_4]^-$ has the least symmetry.

There still remain several frequencies whose origin is uncertain in the very concentrated solutions. They are those appearing at $\Delta\bar{\nu}$ 381, 975, 1120, 1170, and 1360. Two of these are characteristic of sulfur dioxide and one may ascribe its origin to a molecule of the type $\text{SO}_2 \cdot (\text{H}_2\text{O})$. Two others, $\Delta\bar{\nu}$ 381 and 975, are present in fuming sulfuric acid. The stepwise character of the dissociation of sulfuric acid is thus demonstrated by means of the Raman effect. The appearance of some of these lines will become more clear following the discussion of fuming sulfuric acid.

Cartwright has assumed from infrared investigation that, instead of HSO_4 ions, H_3SO_6 ions are produced as a product of the dilution of sulfuric acid. It is apparent from the treatment of the tetrahedral structure of sulfates that this interpretation is somewhat unlikely. Pauling suggests that both $[\text{SO}_4]^{--}$ and $[\text{OH}_4]^{++}$ would have a tetrahedral structure and that the intermolecular forces would cause these radicals to form a quasi-crystalline structure in the liquid. This combination may be grossly represented by



in the acid. While this is by no means to be ignored in the interpretation of the structure of the pure acid, it is to be remembered that these interpretations are based on secondary evidence.

Koteswaram has observed that the effect of raising the temperature of sulfuric acid is approximately the same as dilution. The intensity of $\Delta\bar{\nu}$ 1050 is increased and lines near $\Delta\bar{\nu}$ 558 and 928 are displaced.

To all the foregoing discussion may be added the possibility of a band variously reported as $\Delta\bar{\nu}$ 2985, at $\Delta\bar{\nu}$ 3025 or 3094 and attributed to the O—H vibration by Venkateswaran,¹⁶³⁸ Médard¹⁰⁶⁶ and by Leighton and Burnham⁹⁷⁷ respectively.

Before leaving the discussion of sulfuric acid it should be stated that the technique of the experimental procedure has been greatly improved during the last few years by the addition of a small quantity of potassium permanganate or nitric acid to the concentrated sulfuric acid, which is then distilled. Much confusion had arisen previously because of the great difficulty of measuring distinguishing lines against a strong fluorescent background. This background is apparently caused by the presence of impurities which are removed by the oxidation and distillation procedure mentioned above. As a consequence the more recent data on sulfuric acid are more reliable.

Fuming Sulfuric Acid

It is only natural that after the investigations of sulfuric acid an attempt should have been made to determine something concerning the constitution of fuming sulfuric acid. This was undertaken by Chédin³⁶⁰ and by Gopala Pai.⁶²⁹ These authors come to roughly the same conclusions but differ somewhat in details. Chédin's results are given in Table 69. By progres-

Table 69.—Raman Shifts from Fuming Sulfuric and Sulfuric Acids.

68%	Fuming sulfuric acid, (free SO_3 given in per cent)				10%	Sulfuric acid			
	51%	36%	23%			100%	90%	80%	70%
245(3)	246(1)								
295(1)	297(1)	300(1)	305	315(3)					
330(5)	331(5)	325(5)	327						
			390(3)	388(5)		395(7)			
			427(3)	427(5)		430(7)	412	414	424
484(3)	480(3)	480(1)							
536(5)	535(3)	525(1)							
		565(1)	565(3)	562(5)		560(7)	566	580	583
688(5)	688(1)								
737(5)	740(7)	735(5)	740(3)	735(1)					
		904(3)	915(5)	915(7)		917(8)	915	907	902
957(5)	960(3)	957(3)	975(3)	970(3)		972(3)			
1075(8)	1075(3)						1045	1040	1040
		1160(5)	1160	1140		1140	1148		
1252(8)	1250(7)	1250(7)	1240						
1450(5)	1450(5)	1440(3)	1420	1393	1370				

sively increasing the proportion of sulfur trioxide dissolved in 100-per cent sulfuric acid, the characteristic lines for sulfuric acid gradually disappear and the following new lines occur when "free" sulfur trioxide has reached a theoretical concentration between 10 and 23 per cent, namely, $\Delta\bar{\nu}$ 300, 735, 970, and 1250. Sulfuric acid lines persist until the concentration of sulfur trioxide has reached a value slightly greater than 37 per cent. (Gopala Pai believes that some sulfuric acid lines exist to a much higher concentration.) Between 10 and 36 per cent several new lines have appeared. This behavior, *i. e.*, the appearance of $\Delta\bar{\nu}$ 300, 327, 480, 735, 970, and 1250, is attributable to the formation of $\text{H}_2\text{S}_2\text{O}_7$. The disappearance at approximately 36 per cent of essentially all the lines of sulfuric acid is attributed to the combination of all the sulfuric acid with sulfur trioxide. Between 36 and 51 per cent of SO_3 other lines are seen, namely, $\Delta\bar{\nu}$ 245, 535, 688, and 1075. These are attributed, at least in part, to sulfur trioxide whose principal shifts are $\Delta\bar{\nu}$ 535(3), 1068(8), and 1403(3). In the concentrations employed by Chédin the two strongest lines for S_2O_6 or S_3O_9 , $\Delta\bar{\nu}$ 290(6) and 370(8), also make their appearance. The net result of these observations is the demonstration of the formation of $\text{H}_2\text{S}_2\text{O}_7$ in fuming sulfuric acid and the mixture of free sulfur trioxide and $\text{H}_2\text{S}_2\text{O}_7$ in the more highly concentrated solutions. These results also tend to substantiate the existence

of such shifts in sulfuric acid as $\Delta\bar{\nu}$ 972 and 1140 which have been in some dispute. Furthermore, $\Delta\bar{\nu}$ 735, which has been observed by only a few observers in sulfuric acid, perhaps owes its origin to an excess of sulfur trioxide and possibly forms, therefore, some $\text{H}_2\text{S}_2\text{O}_7$. Apart from the suggested change in the molecular constitution of fuming sulfuric acid and of sulfuric acid itself with dilution or concentration, one other very definite conclusion emerges from this work. Since no observer has noted any characteristic S—H shift, which would appear in the neighborhood of $\Delta\bar{\nu}$ 2600, the usual method of writing sulfuric acid, *i. e.*, H_2SO_4 , cannot be considered otherwise than as a shorthand representation; the hydrogen atoms in sulfuric acid must be attached to oxygen atoms.

Sulfurous Acid

Sulfurous acid has been only slightly investigated. Fadda⁵⁴⁰ obtained a number of lines in solutions of different concentrations. These are $\Delta\bar{\nu}$ 569, 1047, 1142 and 1199,* of which 1142 is the most intense. Nisi¹¹⁷⁸ obtained somewhat similar results and also observed $\Delta\bar{\nu}$ 1337. Practically all these lines are present in sulfuric acid at concentrations less than 100 per cent. Gerding and Nijveld⁵⁸⁷ observed only $\Delta\bar{\nu}$ 531(0), 1150(4), and 1331($\frac{1}{2}$) on dissolving sulfur dioxide in water. It is believed, therefore, that the shift at $\Delta\bar{\nu}$ 569 and 1047 is due to an oxidation of sulfite to sulfate. The remaining lines fall in approximately the same position as in free sulfur dioxide. The intensity of $\Delta\bar{\nu}$ 1142 would seem to substantiate this interpretation. It can, therefore, be concluded that sulfurous acid is essentially a solution of sulfur dioxide in water. This is in agreement with the infrared absorption measurements.

Nitric Acid

This acid was one of the first acids investigated by I. R. Rao.^{1306, 1307} It was studied in concentrations ranging from 65 per cent acid to 9.7 per cent. The most concentrated acid yielded 638, 685, 957, 1046, 1110, and 1299. Of these $\Delta\bar{\nu}$ 638, 685, and 1046 were attributed to the nitrate ion. The remainder, $\Delta\bar{\nu}$ 957, 1110, and 1299, were attributed to the undissociated nitric acid molecule. This is partially an over-simplification. The results are, in general, correct and are given in Figure 63. In this figure the horizontal line at the top of each curve represents complete blackening of the photographic plate. The maxima, marked with a downward arrow, correspond to the undissociated nitric acid molecules, their intensity diminishing so rapidly that they are almost extinct in the fourth curve,

*It should be remembered that in referring to a Raman shift whose exact value is reported slightly differently by various observers, or whose value is changing with concentration, it is frequently expedient to refer to an approximate average of the observed values for the purpose of identification.

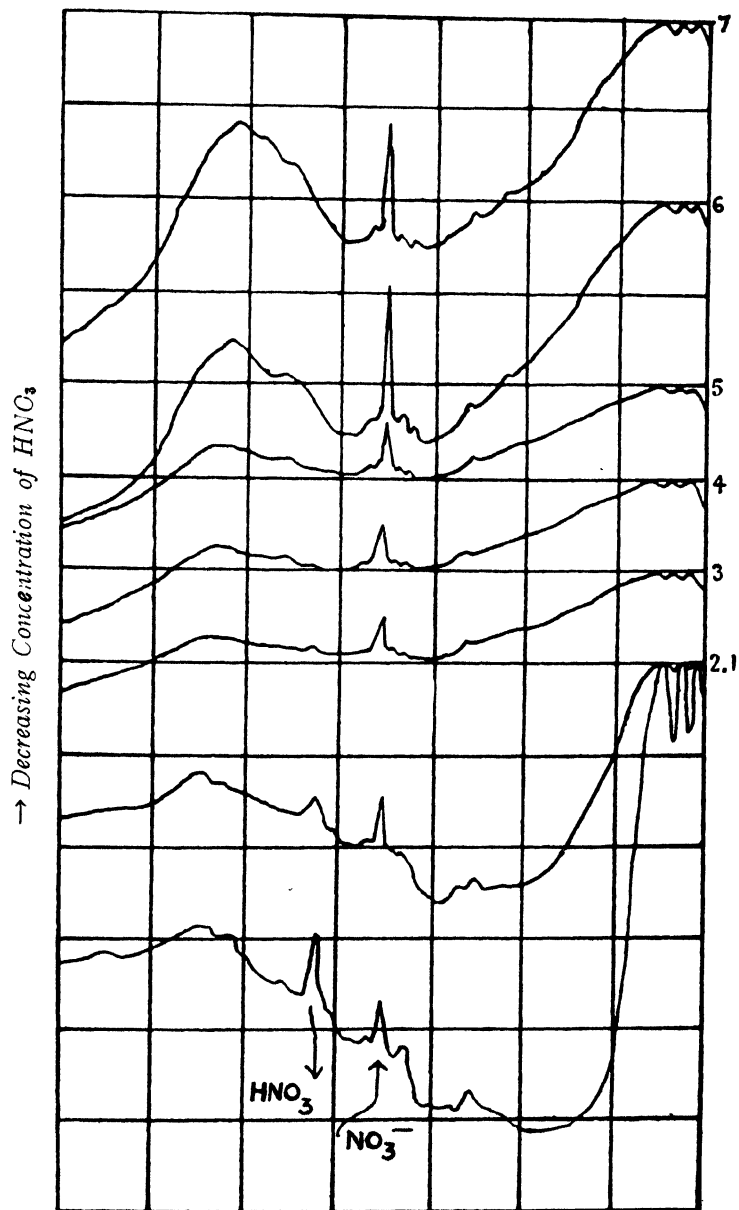


FIGURE 63. The Raman Spectra of Nitric Acid as a Function of Concentration (after I. R. Rao.)

corresponding to a concentration of 39 per cent. The maximum, denoted by an upward arrow, is for the nitrate ion lines, which increase very rapidly in intensity up to 39 per cent concentration. They then diminish again, showing that on initial dilution the dissociation increases much more rapidly than the diminution in concentration, but that after a certain stage the dissociation increase becomes less in proportion to diminution in concentration of the ions. Kinsey⁸¹¹ and Woodward^{1729, 1731} come to very much the same conclusion with slight differences in assignment of frequencies. Dadiou and Kohlrausch⁴³⁶ conclude that the internal oscillations of the nitro-group in organic derivatives lead to the assumption that no inconsiderable proportion of the nitric acid assumes the form $\text{HO}-\text{NO}_2$. Brunetti and Ollano^{293, 294} come to somewhat similar conclusions. They assume that one may have an equilibrium in the acid solution as stated by Hantsch. According to this theory, the addition of water results in the formation of the hydrate of the pseudo-acid, $\text{O}_2\text{N}\cdot\text{OH} \dots \text{H}_2\text{O}$, salts of the hydroxonium type, $(\text{NO}_3)\text{H}_3\text{O}$, salts of the polyhydroxonium type, $(\text{NO}_3)[\text{H}(\text{H}_2\text{O})_n]$, and hydrates of the ions of this salt, $(\text{NO}_3)(\text{H}_2\text{O})^-$ and $[\text{H}(\text{H}_2\text{O})_n]^+$. Hence lines should be found due to the NO_2^- and NO_3^- groups and to nitrate ions and H_3O^+ ions.

The study of nitric acid solutions at varying concentrations is in very much the same position that the study of sulfuric acid was some years ago. There is confusion in the assignment of frequencies to particular types of molecular groups and a certain disparity in the observation and recording of Raman shifts. As the technique for studying sulfuric acid has developed, so improved technique will also be likely to produce more concordant observations in nitric acid studies. At the present moment this is reflected mainly in the investigation of anhydrous nitric acid. A summary of the more recent work on this compound is given in Table 70. This shows

Table 70—The Raman Shifts from Anhydrous Nitric Acid.

Raman Shifts											References
608(3)	679(4)	924(6)	1064(2)	1126(0)	1297(8)	1407(1)	1516(1)	1611(0)	1699(4)		65
612(3)	675(5)	922(8)	1048(1)	1103(1)	1293(10)		1537(3)		1679(8)	3385	1066, 1077
607	667	916			1292			1665	1687	3420	436
607	667	916			1291			1665	1681		4
608	674	922	1050		1295	1400	1516		1672		360
606	668	921	1041		1297		1538	1665	1683		1517

fairly reasonable agreement among different observers. One may suppose that the frequency at approximately $\Delta\bar{\nu}$ 1050 is due to a lack of pure acid. It will be remembered that in the case of sulfuric acid a trace of water may give rise to $\Delta\bar{\nu}$ 1040; hence in nitric acid the presence of a little water may result in $\Delta\bar{\nu}$ 1050, characteristic of the nitrate ion. This $\Delta\bar{\nu}$ 1050 is unobserved or very weakly observed in the anhydrous acid by several workers.

The shift at $\Delta\bar{\nu}$ 1400, observed by some and not by others, may be due to an impurity in the nitric acid as indicated by Médard.¹⁰⁶⁶

Some of the divergence in observed shifts may be ascribed, furthermore, to a variation of the frequencies with concentration or, as is possible in the case of sulfuric acid, to the gradual appearance and disappearance of specific frequencies. It has been shown¹⁰⁷⁷ that $\Delta\bar{\nu}$ 608 in concentrated nitric acid will augment to $\Delta\bar{\nu}$ 657 in 52-per cent acid, and that $\Delta\bar{\nu}$ 674 will increase to $\Delta\bar{\nu}$ 726 in 17.6-per cent acid. There is less variation in the remaining frequencies, but the alteration may amount to as much as 20 wave numbers. At least some of the disagreement between observers may be due, therefore, to an inexact estimate of the nitric acid concentration.

The frequencies observed at $\Delta\bar{\nu}$ 3321,^{1306, 1307} 3385,^{1066, 1077} or $\Delta\bar{\nu}$ 3420⁴³⁶ can be explained as due to water as an impurity or to the $O \leftrightarrow H$ vibration in the $HO-NO_2$ molecule.

It has already been mentioned that dilution of nitric acid causes a change in its spectrum. There is an increase in the Raman frequencies of practically all the lines and a strong increase in the intensity of $\Delta\bar{\nu}$ 1050 on dilution. The only other line which persists at high dilution is $\Delta\bar{\nu}$ 726 (altered from $\Delta\bar{\nu}$ 679). The nitrate ion frequencies generally occurring at $\Delta\bar{\nu}$ 729(2), 1050(10), and 1360(2) are in agreement with the concept that in 50-per cent acid 702, 1053, and 1315 are due to the nitrate ion, if allowance is made for the fact that there is appreciable variation in these shifts among the nitrates themselves. On considering next the more concentrated solutions, it seems that the two frequencies $\Delta\bar{\nu}$ 1537 and 1679 appear only when the concentration is greater than 50 per cent. Organic nitro-compounds yield frequencies near $\Delta\bar{\nu}$ 1270(7), 1340(5), and 1640(8) (although some yield $\Delta\bar{\nu}$ 1550(5)). The alkyl nitrites ($R-O-N=O$) possess $\Delta\bar{\nu}$ 1640(5), and alkyl nitrates 1290(10) and 1644(5) but no strong line at $\Delta\bar{\nu}$ 1050. One may conclude that the nitrate ion differs markedly from the organic nitro-, nitrite or nitrate compounds, whose nitrogen-to-oxygen frequencies are nearer to those of the concentrated acids than to the nitrate ion. Hence the analysis of Dadiou and Kohlrausch⁴³¹ relating the structure of $RONO_2$ -groups to that of the anhydrous acid is somewhat plausible.

It should be recalled that the nitrite ion, whose atoms are situated at the corners of an isosceles triangle,⁹⁶⁷ has the frequencies $\Delta\bar{\nu}$ 813, 1240, and 1331 and probably the structure . The nitrate ion is also triangular (plane equilateral) with the nitrogen in the center. The structure of nitric acid must be radically different from that of nitrate or nitrite ion and more in accordance with $HO-N \begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$ or $HO-N^+ \begin{smallmatrix} \nearrow O \\ \searrow O^- \end{smallmatrix}$ for the reasons already discussed, and it must contain at least one double bond. This is a further indication

of the retention of an actual structural identity in spite of the postulation of resonance phenomena. If this designation of the NO_2 component of this compound is correct, then, as has been shown under organic compounds, the existence of a resonance hybrid does not markedly alter an expected Raman shift.

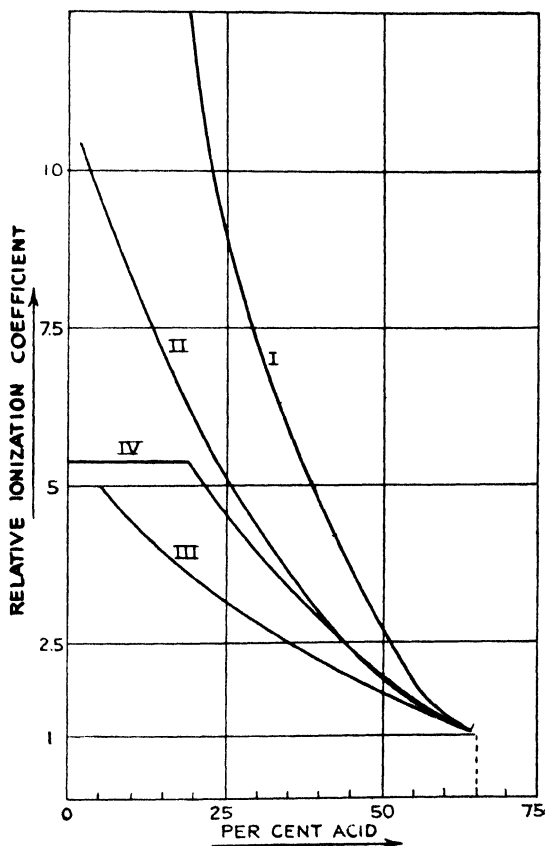


FIGURE 64. The Ionization of Nitric Acid with Dilution (after Chédin).

Venkateswaran¹⁶³¹ believes the ionization process in nitric acid is not indicated by $\text{HO}-\text{N}^+\begin{smallmatrix} \text{O} \\ \diagup \\ \text{O} \end{smallmatrix} \rightarrow \text{H}^+ + \text{O}^-\text{N}^+\begin{smallmatrix} \text{O} \\ \diagup \\ \text{O} \end{smallmatrix}$, which would be unsymmetrical, but by $\text{O}^-\text{N}^+\begin{smallmatrix} \text{O} \\ \diagup \\ \text{O} \end{smallmatrix}$ or $\text{O}^-\text{N}^+\begin{smallmatrix} \text{O} \\ \diagdown \\ \text{O} \end{smallmatrix}$ depending on the system used to indicate coördinate covalence. Polarization measurements indicate that $\Delta\tilde{\nu}$ 920 and 1297 are only slightly depolarized and therefore are parallel or symmetrical vibrations.

The change in intensity of $\Delta\bar{\nu}$ 1050 can be used to measure the degree of dissociation of nitric acid. This is shown in Figure 64 from the work of Chédin.³⁵⁹ Here Curve I represents the relative coefficient of ionization as obtained by I. R. Rao.¹³⁰⁷ Curves II and III represent calculations of this coefficient from the molecular conductivity and viscosity and, finally, Curve IV is obtained from the Raman effect. Above 20 per cent there is fair agreement with the ionization as obtained from viscosity calculations of Kohlrausch.

It is probable that most of the conclusions drawn with regard to the constitution of nitric acid are in accordance with the facts. The Raman effect evidence probably gives a fairly close picture of the ionization process which is somewhat similar to that of sulfuric acid, in the sense that on dilution there is a change from the molecular spectra to the ionic. The divergent results in these experiments are mainly due to ambiguous interpretations and to the failure to use a proper monochromatic source of radiation.

Mixtures of Sulfuric and Nitric Acid and Nitrogen Pentoxide

Before discussing the results obtained with mixtures of nitric and sulfuric acids it is necessary to discuss the spectra obtained from nitrogen pentoxide. Chédin³⁶⁰ observed that on treating anhydrous nitric acid with phosphorus pentoxide there are three lines of the nitric acid which are strongly reinforced. These are $\Delta\bar{\nu}$ 1040(5), 1120(2), 1401(8), where the intensities are given in terms relative to each other. This leads to the study of crystalline nitrogen pentoxide. From these crystals were obtained $\Delta\bar{\nu}$ 1050 and 1400. Mixtures of nitric acid and nitrogen pentoxide were next investigated; the concentration of nitrogen peroxide was varied from 8 to 21 per cent. Here again the two lines $\Delta\bar{\nu}$ 1050 and 1400 increased progressively in intensity. Susz and Briner¹⁵¹⁷ obtained similar results.

However, a similar investigation of the pentoxide in organic solvents yielded $\Delta\bar{\nu}$ 870(3), 1244(5), 1335(2). Experiments employing phosphorus oxychloride as a solvent yielded $\Delta\bar{\nu}$ 1249 and 1337. The difference between the spectra obtained from organic solvents or phosphorus oxychloride and those observed with the crystals or in nitric acid solution is accounted for on the basis of polymerization of the pentoxide, with the polymer existing in the crystals and in the nitric acid solutions.

The principal frequencies for nitrogen pentoxide having been established, the Raman spectrum obtained from mixtures of nitric and sulfuric acids becomes more intelligible. A combination between nitric and sulfuric acids has long been supposed to yield several types of compounds from $10\text{SO}_3 \cdot \text{N}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ to $\text{N}_2\text{O}_5(\text{SO}_3)_4 \cdot \text{H}_2\text{O}$. The constitution of none of these compounds has been satisfactorily established. The investigations of

Chédin throw considerable light on the possible constitution of nitric and sulfuric acid mixtures. The first experiments carried out were on mixtures of varying concentrations of nitric acid and fuming sulfuric acid containing 60 per cent sulfur trioxide. It will be recalled that at 60 per cent sulfur trioxide, fuming sulfuric acid consists entirely of $\text{H}_2\text{S}_2\text{O}_7$ and some free sulfur trioxide. The results obtained from these experiments are indicated in Figure 65 where only the principal lines involved are shown.

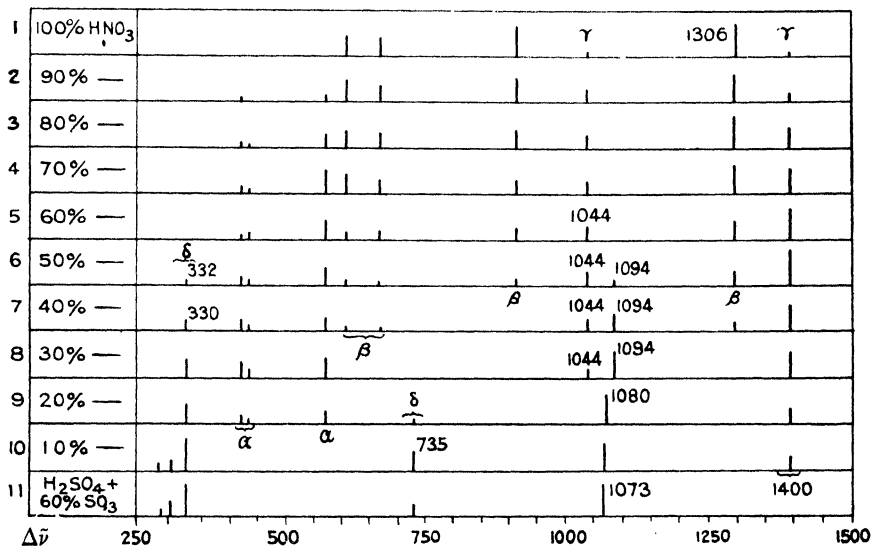


FIGURE 65. The Raman Shifts from Mixtures of Sulfuric Acid, Nitric Acid and Sulfur Trioxide (after Chédin). Sulfuric acid is designated by α , nitric acid by β , nitrogen peroxide by γ , and pyrosulfuric acid by δ .

In Column 11 the principal lines present are those at $\Delta\bar{\nu}$ 300, 327, and 735 due to $\text{H}_2\text{S}_2\text{O}_7$, and at 1073, originating in the excess sulfur trioxide. As the amount of nitric acid is increased and the fuming sulfuric acid decreased there appear additional lines due to sulfuric acid, while at the same time those corresponding to $\text{H}_2\text{S}_2\text{O}_7$ gradually decrease in intensity. Immediately on addition of nitric acid the shift at $\Delta\bar{\nu}$ 1400 corresponding to nitrogen pentoxide appears and the sulfur trioxide frequency at $\Delta\bar{\nu}$ 1073 is appreciably increased in magnitude. $\Delta\bar{\nu}$ 1400 for the nitrogen pentoxide passes through a maximum near 60 per cent nitric acid after which it diminishes. From a little over 30 per cent nitric acid, the other lines typical of the anhydrous acid increase in intensity while those for sulfuric acid decrease. There are no lines for the pyrosulfuric acid after 50 per cent. At 30 per cent nitric acid $\Delta\bar{\nu}$ 1044, the other line for nitrogen pentoxide, appears and

increases in intensity until a nearly 50 per cent mixture is reached after which it, like $\Delta\bar{\nu}$ 1400, decreases. The line which originally corresponded to free sulfur trioxide and which is finally augmented to $\Delta\bar{\nu}$ 1094 is no longer visible after a 50-per cent solution is reached.

The explanation given for this behavior is as follows. Beginning with 100-per cent nitric acid the addition of a small proportion of sulfuric acid produces first the spectrum of a mixture of nitric acid, sulfuric acid and nitrogen pentoxide which originates in the dehydration of the nitric acid. This process continues, sulfuric acid and nitrogen pentoxide spectra increasing in intensity and the nitric acid spectrum decreasing on account of a dilution effect, until at a 50-per cent solution the lines for pyrosulfuric acid appear and also a new line at $\Delta\bar{\nu}$ 1094. When the fuming sulfuric acid concentration has reached 70 per cent, there no longer remain any lines for nitric acid, as it is completely dehydrated. At only 20 per cent nitric acid and 80% fuming sulfuric acid the shift for 1045 of nitrogen pentoxide disappears and the frequency at $\Delta\bar{\nu}$ 1094 is displaced by about 20 wave numbers to $\Delta\bar{\nu}$ 1080, which is close to the spectrum of pure sulfur trioxide. The relative behavior of $\Delta\bar{\nu}$ 1094 and 1044 is attributed to an association between nitrogen pentoxide and sulfur trioxide. When there is free nitrogen pentoxide present, $\Delta\bar{\nu}$ 1044 will appear and remain but, if there is sufficient sulfur trioxide to combine with all the nitrogen pentoxide present, then at least one of the normal vibrations of nitrogen pentoxide will be modified by the change in symmetry of the molecule. This is reflected also in the modification of the normal vibration of the sulfur trioxide which approaches the normal when the nitric acid concentration represents only a small fraction of the total.

The next variation to consider is the behavior of mixtures of nitric acid and a sulfuric acid-sulfur trioxide combination which contains 35 per cent of sulfur trioxide. Actually, as has been pointed out previously, when sulfur trioxide is added to sulfuric acid in quantities amounting to less than 36 per cent, no free sulfur trioxide is present. The results are shown in Figure 66, where only the principal lines are used. The 100-per cent fuming sulfuric acid as expected shows no line at $\Delta\bar{\nu}$ 1075 for free sulfur trioxide. The addition of 10 per cent of nitric acid produces immediately the $\Delta\bar{\nu}$ 1400 line for nitrogen pentoxide and 1084, which, as has been postulated, is the line characteristic of the $\text{N}_2\text{O}_5 \cdot \text{SO}_3$ complex. The remaining lines are due to sulfuric and pyrosulfuric acids. The appearance of this pentoxide-trioxide combination in a mixture which contained free sulfur trioxide to begin with, is explicable on the assumption that some of the sulfur trioxide formerly combined with sulfuric acid as pyrosulfuric acid is released to combine with the pentoxide by the dehydration of the nitric acid. The remainder of the picture is somewhat like that described previ-

ously with 60 per cent of free sulfur trioxide. The lines for nitric acid appear at lower concentrations because of the greater concentration of nitric acid as compared with potentially, but not actually, free sulfur trioxide. For a similar reason, the line for free sulfur trioxide disappears and that for free nitrogen pentoxide appears at a lower nitric acid concentration. Those corresponding to pyrosulfuric acid disappear above 10 per cent nitric acid in lieu of 50 per cent with the more concentrated fuming sulfuric acid solution.

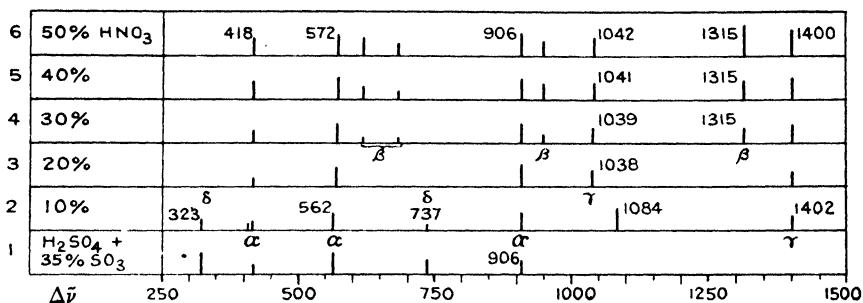


FIGURE 66. The Raman Spectra from Sulfuric Acid containing 30 Per Cent Sulfur Trioxide; and from Nitric Acid at Varying Concentrations in this Mixture (after Chédin). The designations by means of Greek letters have the same significance as in Figure 65.

If to a mixture of sulfuric acid and 45 per cent of sulfur trioxide, nitric oxide is added corresponding to 10, 20 and 30 per cent, the following is the result. First, there is the appearance of $\Delta\bar{\nu}$ 1080 corresponding again to the $\text{N}_2\text{O}_5 \cdot \text{SO}_3$ complex and appearance of the stronger characteristic lines of sulfuric acid. It is to be borne in mind that the 45 per cent excess sulfur trioxide has entirely combined with the sulfuric acid to produce pyrosulfuric acid. The addition of 10 per cent of nitric acid therefore breaks down some of the pyrosulfuric acid into sulfuric acid and the pentoxide complex. With 20 per cent of nitric acid there is a still further decrease in the pyrosulfuric acid concentration and an increase in the amount of sulfuric acid present. At 30 per cent of nitric acid this same increase and decrease in concentrations of the sulfuric and pyrosulfuric acid components continue but, in addition, there appears the expected frequency at $\Delta\bar{\nu}$ 1040 corresponding to uncombined nitrogen pentoxide. As has been pointed out previously, when the nitric acid concentration has reached a point where it is dehydrated by means of sulfur trioxide in pyrosulfuric acid ($\text{H}_2\text{SO}_4 + \text{SO}_3$) and has utilized all or nearly all of this potentially free sulfur trioxide the $\Delta\bar{\nu}$ 1090 will begin to disappear and the $\Delta\bar{\nu}$ 1040 frequency will undoubtedly be manifested.

This behavior is further substantiated by the result obtained by adding nitrogen pentoxide alone to sulfuric acid solutions containing 35 per cent of sulfur trioxide. The addition of 10 per cent of nitrogen pentoxide produces the complex frequencies near $\Delta\bar{\nu}$ 1090 and 1400. A further increase in the pentoxide concentration indicates the presence of the $\text{SO}_3 \cdot \text{N}_2\text{O}_5$ complex, free nitrogen pentoxide, some pyrosulfuric acid and sulfuric acid. This indicates that there is a point beyond which the sulfur trioxide may not be removed from pyrosulfuric acid over a certain range of concentration. The subsequent disappearance of the $\text{SO}_3 \cdot \text{N}_2\text{O}_5$ complex line in nitric acid solutions is presumably to be attributed to a combination of this sulfur trioxide with the water obtained from nitric acid in the formation of more nitrogen pentoxide.

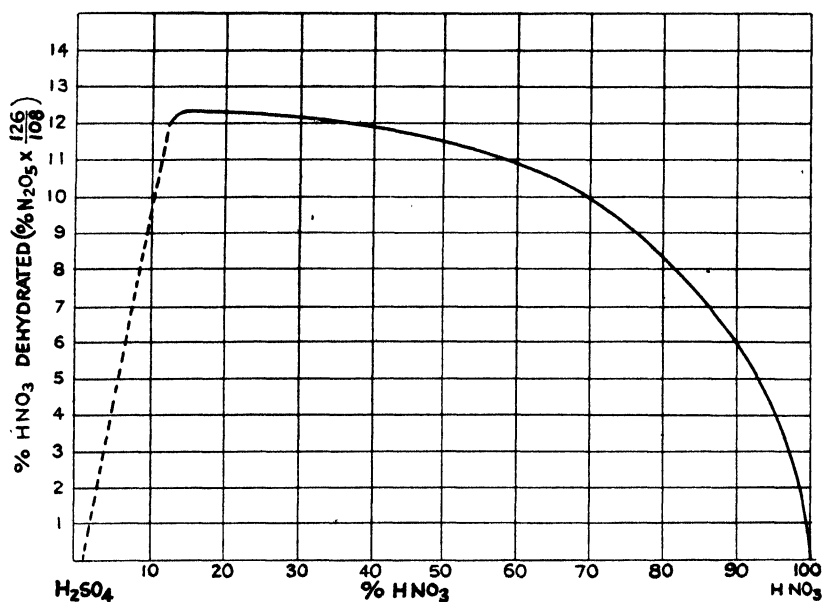


FIGURE 67. The Formation of Nitrogen Peroxide by the Dehydration of Nitric Acid (after Chédin).

The interpretation of these investigations on fuming sulfuric acid and nitric acid mixtures may be extended to the study of mixtures of sulfuric and nitric acids. These results are given in Figure 67 and indicate the dehydration of nitric acid with the production of nitrogen pentoxide. The maximum amount of nitrogen pentoxide produced is approximately 12½ per cent at 15 per cent of nitric acid.

It has been shown through the investigations of mixtures of nitric,

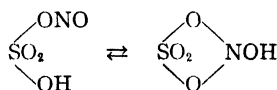
sulfuric and fuming sulfuric acids that the precise constitution of the resulting mixtures varies with the relative concentration of the components. These changes in constitution may be investigated in semiquantitative fashion and such investigation has provided considerable insight into this complex question from a chemical point of view. The Raman spectra approach has been particularly helpful from a theoretical point of view but also is of interest commercially so far as nitration of various organic compounds is concerned.

Nitrosylsulfuric Acid

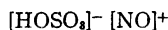
Although it is usually agreed that the empirical formula of nitrosylsulfuric acid is HNSO_5 , there is a diversity of opinion concerning its molecular configuration. Several different molecular structures have been proposed, as follows:



Nitroxylsulfonic acid.



Nitrosylsulfuric acid.



Nitroacidium sulfate.

It will be seen presently which, if any, of these will agree with the Raman spectra data. Angus and Leckie^{64, 65} have determined the spectra of solid HNSO_5 and a solution of the compound in 98-per cent sulfuric acid. Nitrosylsulfuric acid yields the following Raman shifts:

HNSO ₅ (solid)				
428(1)	560-608(3)	720(4)	811(1)	922(4)
992(0)	1041(4)	1164(3)	1286(4)	1392(1)
1485(3)	1592(0)	1687(0)	2311(9)	

It is to be noted that several of the frequencies given find their counterpart in the spectra obtained from both sulfuric and nitric acid themselves. Most conspicuous of these are the lines occurring near $\Delta\tilde{\nu}$ 420, 560, 916, 1140, and 1365 present in sulfuric acid and 607, 920, 1050, 1297, and 1699 present in nitric acid. This leaves $\Delta\tilde{\nu}$ 720(4), 811(1), 1485(3), 1592(0), and 2311(9) as distinguished from either of the other two acids. The frequencies at $\Delta\tilde{\nu}$ 992(0) and 1286(4) are possibly characteristic frequencies. There is an apparent decrease in the magnitude of the two shifts $\Delta\tilde{\nu}$ 720 and 811 for nitrosylsulfuric acid which occurs in a 98-per cent sulfuric acid solution of the compound if the sulfuric acid is diluted to 75 per cent. Most

striking is the frequency at $\Delta\bar{\nu}$ 2311. This is the strongest line of all and persists in partially diluted sulfuric acid solutions of nitrosylsulfuric acid. This falls in the region which has been assigned to triple-bond structures. Angus and Leckie conclude that nitrosylsulfuric acid has the nitroacidium sulfate structure $[\text{HOSO}_3]^- \text{NO}^+$ proposed by Hantsch and Berger. This is based partially on the increase in intensity of $\Delta\bar{\nu}$ 1045 in the more dilute sulfuric acid solutions. This points to the presence of an HSO_4 group. While it is true that nitric oxide alone has a frequency of only $\Delta\bar{\nu}$ 1877, it is possible that NO^+ may have a frequency in $\Delta\bar{\nu}$ 2311 as it is isoelectronic with nitrogen. The appearance of $\Delta\bar{\nu}$ 2311 was observed also by Chédin⁵⁵⁵ who noticed that this line was present when a solution consisting of approximately 10 per cent nitric and 90 per cent sulfuric acids (containing a small quantity of water) is boiled and then cooled. This was attributed to nitrosylsulfuric acid by Chédin.

None of these explanations takes into consideration the frequencies presumably appearing at $\Delta\bar{\nu}$ 1485, 1592, and 1687 in solid nitrosylsulfuric acid. The latter two are quite weak and may be due either to nitric acid as an impurity or possibly to an equilibrium among more than one structural form. The frequency at $\Delta\bar{\nu}$ 1485 which occurs with fair intensity in the solid is more characteristic of a transverse oscillation of an H—N group than of anything else. It is also noticeable that at least three of the HNSO_3 frequencies are fairly close to those observed with the nitrate ion ($\Delta\bar{\nu}$ 729, 1050, and 1360) which are not present in concentrated nitric acid.

As has been mentioned under the discussion of nitric acid, the alkyl nitrates, nitrites, and nitro- compounds all have strong frequencies near $\Delta\bar{\nu}$ 1650. One is led to conclude, therefore, with Angus and Leckie that the nitroxylsulfonic type of structure is less plausible and that the nitroacidium sulfate structure may be possible. If this were the case there would seem to be no obvious reason for a close similarity between the organic nitrites, nitrates and nitroacidium sulfate.

Perchloric Acid and its Salts

Other inorganic acids such as perchloric^{65, 482, 555, 1175, 1189, 1191, 1532} have been investigated. The Raman spectra of perchloric acid and some of the perchlorates are indicated in Table 71. In general the spectrum of perchloric acid has not differed widely from that of the perchlorates. This, however, may be somewhat similar to the behavior of other acids and their salts at different concentrations. According to Fonteyne⁵⁵⁵ the Raman spectra of absolute perchloric acid is different from that of the acid in solution, although up to a 70-per cent solution the spectra of the perchlorates and the acid are approximately identical. There is apparently a

Table 71.—The Raman Shifts from Perchloric Acid and Some Perchlorates and Periodates.

Compounds	Raman Shifts				
HClO ₄ (Liq.)				422(1)	570(5)
HClO ₄ (Sol.)					461(1)
LiClO ₄ (Sol.)					450(3)
NaClO ₄ (Sol.)					463(1)
KClO ₄ (Sol.)					461(1)
NH ₄ ClO ₄ (Sol.)					463(1)
KIO ₄ (Sol.)					
KIO ₄ (Cryst.)	277($\frac{1}{2}$)	295($\frac{1}{2}$)	337(2)	349(1)	
HClO ₄ (Liq.)		730(5)		922(0)	1025(4) 1190
HClO ₄ (Sol.)	627(1)			936(3)	1118(3)
LiClO ₄ (Sol.)	620(3)			922(3)	1110(1)
NaClO ₄ (Sol.)	626(1)			935(8)	1120(1)
KClO ₄ (Sol.)	632(1)			936(7)	
NH ₄ ClO ₄ (Sol.)	629(0)			930(6)	1109(1)
KIO ₄ (Sol.)		702(5)		841(1)	
KIO ₄ (Cryst.)		736(0)	795(10)	828(0) 842(3)	851(1)

marked change in the spectrum of the acid as the concentration is increased. The spectrum of pure perchloric acid shows four main lines corresponding to $\Delta\bar{\nu}$ 570(5), 730(5), 1026(4), 1119(1). The relative intensities of these lines do not differ much from the intensities observed for the perchloric ion. The magnitudes of the shifts, however, are quite different. In addition to the lines mentioned, the appearance of a line at $\Delta\bar{\nu}$ 422 is attributed to the presence of an acidium salt connected with an associated perchloric acid molecule. Several chemical schemes are proposed to explain these variations, including polymerization of perchloric acid and ionization of the polymer into a perchlorate ion and a complex compound. None of these explanations can be justified by the Raman spectra alone. Certainly an increased complexity of the molecular aggregate would increase the number of Raman lines. The listing of chemical reactions by means of chemical formulas does not necessarily interpret Raman spectra results. It is clear, however, that there is a profound change in the spectrum of perchloric acid with dilution. This change, as Fonteyne has pointed out, is in the direction of the diminution of the force constant of the typical perchlorate bond. There is no obvious explanation from these data of the absence of an $\text{H}\leftrightarrow\text{O}$ oscillation such as has been observed in other acids of this type. Simon and Reuther¹⁴⁴¹ however, claim $\text{O}\leftrightarrow\text{H}$ bands from $\Delta\bar{\nu}$ 3245 to 3420 in addition to $\Delta\bar{\nu}$ 322 not observed by others for perchloric acid. In this case a pyramidal molecule results with three oxygen atoms as the base, the chlorine atom at the center of gravity, and one hydroxyl group at the apex representing the pseudo-form. The

perchlorate ion is tetrahedral and should give rise to four Raman frequencies, two triply degenerate and one doubly degenerate. Recently Fonteyne has stated that the Raman spectra of HClO_4 confirms the existence of HOClO_3 (symmetry C_{3v}) when the acid content in solution exceeds 73 per cent. This view is also held by Simon. Raman lines found for the ClO_3 group are also present in the spectrum of Cl_2O_7 . The valence angle of the $\text{Cl}-\text{O}-\text{Cl}$ arrangement is computed to be 128° . This is largely hypothetical.

Iodic Acid and Derivatives

Iodic acid and its derivatives have been investigated by a number of workers.^{482, 910, 1162, 1163, 1175, 1623, 1729, 1731} The most complete studies of iodic acid and its salts have been undertaken by Nayar and Gairola,¹¹⁶² Nayar and Sharma,¹¹⁶³ Venkateswaran¹⁶²³ and by Kujumzelis.

Disregarding for the moment the hydrogen atom and considering the iodate ion, there are two possible symmetries. One of these is the D_{3h} type similar to the nitrate ion. The oxygen atoms would be at the corners of the equilateral plane triangle and the iodine atom in the center. In the other case the symmetry would be the C_{3v} type with the oxygen atoms situated at the corners of the base of a pyramid and the iodine atom at the apex. The first of these symmetry types would give rise to three fundamental Raman frequencies, one of which is polarized and two depolarized. The other symmetry type, being pyramidal, would give rise to four Raman frequencies, two of which would be doubly degenerate and depolarized and two symmetrical and polarized. In Table 72 is shown the Raman spectra of iodic acid and iodates. It is readily seen that there is a superabundance of Raman frequencies. Since few polarization data are available, it is not possible to designate with absolute accuracy the types of vibration which these frequencies represent. Some of them may be combination frequencies. The frequency at $\Delta\bar{\nu}$ 1392 may represent a combination between $\Delta\bar{\nu}$ 780 and 635, and the frequencies occurring near $\Delta\bar{\nu}$ 640 may be the overtone of $\Delta\bar{\nu}$ 328. The intensity relationships, however, are not very compatible with this suggestion.

Originally it was presumed by Woodward¹⁷³¹ that a 10*N* solution of the acid was completely dissociated. However, Venkateswaran¹⁶²³ believes that the dissociation is incomplete even for concentrations of 0.5*N*. Some of the intensity lines observed in crystalline iodic acid become broad and intense bands in solution. The frequencies at $\Delta\bar{\nu}$ 328, 377, 633, 713, and 782 are attributed to the iodic acid molecule. The first two of these on solution are replaced by a wide band whose maximum is near $\Delta\bar{\nu}$ 334 but whose width covers nearly 50 wave numbers. The $\Delta\bar{\nu}$ 413 disappears completely and is replaced by $\Delta\bar{\nu}$ 463 in the stronger solutions. The frequency

at $\Delta\bar{\nu}$ 633 broadens somewhat but is otherwise unchanged in the more concentrated solutions. The $\Delta\bar{\nu}$ 713, which appears strongly in the crystal, disappears on solution. The sharp line at $\Delta\bar{\nu}$ 782 is replaced by an immensely broad combination of bands extending over a distance of nearly 100 wave numbers. On dilution it is noticed first that the band appearing near $\Delta\bar{\nu}$ 334 becomes less in intensity and is much sharpened. The group of bands whose maximum is at $\Delta\bar{\nu}$ 779 in the concentrated solution narrows on dilution and is shifted to a slightly higher frequency. At a concentration corresponding to $6N$ there appears, superimposed on these bands, an additional line at $\Delta\bar{\nu}$ 796 which increases in intensity with further dilution. The band at $\Delta\bar{\nu}$ 463 disappears when the concentration is less than $6N$. The $\Delta\bar{\nu}$ 633 is removed entirely when this solution reaches less than $0.5N$.

In comparing these results with those obtained from solutions of iodates, it is evident that these changes represent a stepwise dissociation into the iodate ion but that dissociation is incomplete even in the fairly dilute solutions. Potassium biiodate has a spectrum which is characteristic of both the iodate ion and the undissociated acid. The strong frequencies at $\Delta\bar{\nu}$ 713 and 377 for the crystalline acid are missing. On the other hand $\Delta\bar{\nu}$ 818, which is extremely weak in the acid and strong in the iodate ion, is strong in the biiodate. The two frequencies which persist in the iodate solutions are those near $\Delta\bar{\nu}$ 795 and 325. These, however, are too few to represent the entire spectrum of the iodate ion. One cannot say with certainty that $\Delta\bar{\nu}$ 423 and 603 are the missing frequencies of the pyramidal structure. The multiplicity of frequencies occurring in the crystalline iodates is probably the result of a splitting of the degenerate frequencies. It is shown elsewhere that this frequently occurs when, for any reason, the symmetry of the molecule is disturbed.

Nayar and Sharma ¹¹⁶³ and Nayar, Srivastava, Sen, Gopal and Sharma contend that solid iodic acid and the concentrated solutions which are polymerized give rise to a change in spectrum due to polymerization. It is also maintained by Nayar and Gairola ¹¹⁶² that there is no evidence for the existence of a bivalent ion, I_2O_6 . Nayar and Sharma contend that the failure to elicit $\Delta\bar{\nu}$ 334 and 634 in the very dilute solutions of the acid is evidence of the existence of the polymer of the acid. These lines, however, have been noted by Venkateswaran even in dilute solutions of the acid. Furthermore, at least one of them appears in dilute solutions of the iodates. It is more likely that, if there is any polymerization, it is in the direction of the production of I_2O_6 ions. This is indicated somewhat by the appearance of $\Delta\bar{\nu}$ 823 in the concentrated solution. This frequency coincides with $\Delta\bar{\nu}$ 818 for the biiodate which possesses an I_2O_6 -group.

Venkateswaran suggests that the large group of low-frequency oscillations less than $\Delta\bar{\nu}$ 328 in the crystal is possibly due to lattice vibrations,

that is, they are connected with vibrations of the layers of the atoms in crystal lattice against each other. In agreement with Venkateswaran, it is not difficult to believe that vibrations of this type would give rise to as many separate lines. An equal number, however, have been noted in the case of calcite and baryte. The alternative hypothesis is one which would ascribe these oscillations to hindered rotation of the molecules in the solid state.

A consideration of the total evidence concerning iodic acid would indicate a stepwise ionization process in solution. This never reaches completion. In the more concentrated solution there is, first, un-ionized iodic acid or iodic acid polymer. On further dilution the polymer becomes a monomer producing iodate ions. Notwithstanding the lack of sufficient polarization data and the lack of an adequate number of frequencies in dilute solution, the evidence would seem to indicate a pyramidal form of the molecule, two of the fundamental frequencies ν_4 and ν_1 being near $\Delta\bar{\nu}$ 332 and 790 respectively. The frequency $\Delta\bar{\nu}$ 630 (or 460) represents ν_3 and $\Delta\bar{\nu}$ 820 corresponds to ν_2 . At least some of the frequencies near $\Delta\bar{\nu}$ 800 are combination frequencies. The real truth of the matter—without rationalization—is that the experimental evidence is inadequate to indicate the proper frequency assignments. From the published data one can not be certain that ν_3 is greater than ν_1 or vice versa.

Acids of Phosphorus and Their Salts

Phosphoric acid, the other acids of phosphorus and their salts in general may be grouped into three categories, namely, those which may contain a PO_2 ion, a PO_3 ion, or a PO_4 ion. Intermediate between these groups are those compounds which as a result of incomplete substitution still retain one or two atoms of hydrogen. Just as the hydrogen sulfates may differ from the true sulfates or sulfuric acid, so the equivalent hydrogen or dihydrogen phosphate may differ from the true *ortho*-phosphoric acid or sodium *ortho*-phosphate. Somewhat unlike the sulfuric acid compounds, the derivatives of phosphoric acids have spectra which differ appreciably from that of the acid. These acids and their compounds have been subjected to a fair amount of investigation. Most of this procedure has been qualitative rather than quantitative. In the history of Raman studies this has been useful but, in a critical survey of the results obtained, more emphasis will be placed on the work of Simon and Fehér¹⁴⁴⁰ and of Venkateswaran.¹⁶²⁸ To make clear, however, the divergence of opinion in regard to the phosphates, there are submitted in Table 73 the results of most of the investigators in that field.

Table 73.—The Raman Shifts from Phos

Substances		Raman Shifts						
H ₂ PO ₄ (sol.)	356(3)		495(1)					905(3)
		361(0)	495(1)			886(8)		919(10)
NaH ₂ PO ₄ (sol.)	358(1)			518(2)	810	899(6)		959(1)
NaH ₂ PO ₄ (sol.)	356(1)		495(1)			886(8)		950
KH ₂ PO ₄ (sol.)						882(6)		
KH ₂ PO ₄ (sol.)	360(1)			510(1)		869(6)		
KH ₂ PO ₄ (sol.)		402(4)		523(4)		893(7)		
NH ₄ H ₂ PO ₄	360(1)			515(0)		885(6)		
Na ₂ HPO ₄ (sol.)						886(0)		971(3)
K ₂ HPO ₄ (sol.)		400(4)		532(4)		867(1)		980(7)
K ₂ HPO ₄ (sol.)						889(1)		965(5)
NH ₄ NaHPO ₄ (sol.)				515(0)		889(0)		975(4)
(NH ₄) ₂ HPO ₄	363(0)			515(0)		889(1)		975(6)
(NH ₄) ₂ PO ₄ (sol.)							924(2)	
(NH ₄) ₂ PO ₄ (sol.)	363			515(0)				985(4)
(NH ₄) ₂ PO ₄ (cryst.)							951(2)	
K ₃ PO ₄ (sol.)		400(4)		557(1)			935(8)	
K ₃ PO ₄ (sol.)							944(3)	984(5)
K ₃ PO ₄ (cryst.)							944(2)	966(2)
Na ₃ PO ₄ (sol.)							937(8)	
Na ₃ PO ₄ (sol.)								971(5)
Na ₃ PO ₄ (cryst.)							956(2)	
NaBePO ₄ (cryst.)	232(0)	353(1)	416(4)	463(4)	572(0)	612(1)		
Ca ₃ [FCl](PO ₄) ₂ (cryst.)			443(2)		592(2)			966(6)
H ₂ PO ₃ (sol.)			425(4)		523(2)			946(8)
H ₂ PO ₃ (sol.)						672(5)		940(4)
H ₂ PO ₃ (cryst.)								961(6)
KH ₂ PO ₃ (sol.)			441(4)		548(0)			916(4)
NaH ₂ PO ₃ (sol.)						642(5)		925(2)
K ₂ HPO ₃ (sol.)				458(4)	551(0)			982(6)
Na ₂ HPO ₃ (sol.)						893(3)		978(3)
Na ₂ HPO ₃ (cryst.)							961(3)	
Na ₄ P ₄ O ₁₃ (sol.)								
H ₂ PO ₂		429(4)				794(1)		927(5)
NaH ₂ PO ₂			470	588(0)		827(1)		921(5)

Phosphoric Acid

In phosphoric acid there is an apparent displacement of the magnitude of the strongest frequency corresponding to the symmetrical oscillation of the PO₄-group in the tetrahedral structure. This acid behaves very much the same as sulfuric acid; there is a pronounced change in the magnitude of the shift occurring at $\Delta\tilde{\nu}$ 914(8) in the 85-per cent solution, which is reduced to $\Delta\tilde{\nu}$ 880(8) in the 83-per cent solution. As the concentration of acid is diminished there is an apparent appearance of the four frequencies at $\Delta\tilde{\nu}$ 960, 1082, 1194, and 1427, whose intensities are approximately (1). According to Venkateswaran¹⁶²⁸ the shift near $\Delta\tilde{\nu}$ 1080 occurs uniformly in the primary, secondary and tertiary substituted compounds. This is probably due to the phosphate ion since it occurs only in a dilute solution of the acid (15-per cent) and in the salts of the acid. In the

phorus Acids and Their Salts

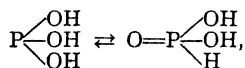
Raman Shifts				References
		1100(1)		113, 779, 1066
	1082(1)	1194(1)	1427(1)	37
	1061(2)			1628
	1085(3)			119, 1175
	1071(5)			1628
	1080(5)			691
1023(4)	1079(4)			1628
	1090(3)			1440
	1085(4)			1628
	1092(1)	1236(1)		1628
	1070(1)			1440
	1085(1)			1628
	1070(1)			1628
				1414
	1080(0)			1628
				1628
				1440
				1628
				1628
				1440
	1085(0)			1628
				1628
1010(7)	1044(1)	1069(1)		1181
	1044(0)			1181
1014(3)			2485(8)	1440
1012(2)				598
1038(2)		1104(1)	2485(8)	2511(7)
1031(6)			2396(6)	1440
	1068(5)			598
1029(4)			2314(6)	1440
1030(1)				598
	1046(1)	1057(1)	2338(6)	37
		1137(2)		598
		1072(1)	2415(8)	1440
		1127(5)		
	1047(6)	1088(0)	2353(8)	2450(1)
		1153(5)		1440

secondary and tertiary substituted compounds there appears $\Delta\bar{\nu}$ 975(5) which does not appear in the pure acid. The frequency at $\Delta\bar{\nu}$ 886–914 in the pure acid occurs with decreased intensity as substitution takes place. The remaining frequencies are relatively constant. The application of this information derived from the salts of phosphoric acid apparently indicates a stepwise dissociation of phosphoric acid into H_2PO_4 ions and finally into HPO_4 ions. The amount of HPO_4 ions is significant even in a dilute solution.

Phosphorous Acid

While phosphorous acid may be prepared by the reaction of phosphorus trichloride with water there has been some doubt, from a chemical standpoint, regarding the tribasic nature of the product. It has been assumed

that there may be an equilibrium between the forms designated by



in view of the fact that only two of the hydroxyl hydrogen atoms are replaceable by metals.

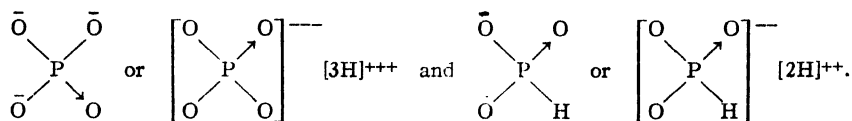
The results from Raman spectra investigations of the primary and secondary phosphorus acids lead to interesting conclusions. Anantha-krishnan,³⁷ Ghosh and Das⁵⁹⁸ and Simon and Fehér¹⁴⁴⁰ are among those who have contributed most extensively to this phase of inorganic structure. Their results are summarized in the second half of the table showing the phosphorous acid Raman shifts. Because there is a difference of opinion between workers all the results are given. The most striking feature is the presence of the shifts from $\Delta\tilde{\nu}$ 2300–2500. The interpretation of this is obvious when one considers the other well-known hydrogen shifts. Some of these are as follows:

Table 74.—Some Typical Inorganic R—H Shifts.

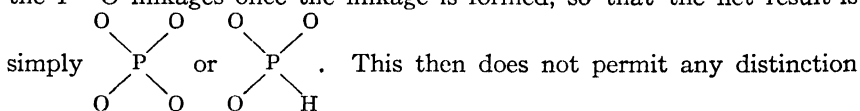
Linkage	Raman Shift	Source
C—H	2920	CH ₄
S—H	2525	H ₂ S
O—H	3630	NaOH
N—H	3334	NH ₃
P—H	2306	PH ₃
Cl—H	2885	HCl
Se—H	2312	H ₂ Se
Si—H	2187	SiH ₄

In phosphorous acid only a P—H vibration could give rise to a frequency near $\Delta\tilde{\nu}$ 2300–2500. From its intensity this eliminates any large proportion of $\text{P} \begin{array}{c} \text{OH} \\ \diagup \\ \text{OH} \end{array}$. This leaves then three possibilities: $\text{O}=\text{P} \begin{array}{c} \text{OH} \\ \diagdown \\ \text{H} \end{array}$,

$\text{O} \leftarrow \text{P} \begin{array}{c} \text{OH} \\ \diagup \\ \text{H} \end{array}$, and $\left[\text{O} \begin{array}{c} \diagup \\ \text{O} \diagdown \end{array} \text{P}-\text{H} \right]^- [2\text{H}]^{++}$. Although Médard¹⁰⁶⁶ claims there is present an OH shift near $\Delta\tilde{\nu}$ 3360–3700 in phosphoric acid, no one else has observed one in water-free phosphoric, phosphorous, or hypophosphorous acids. The absence of this shift may be apparent rather than real, and due to a difficulty in eliciting the shift as is the case with the higher alcohols. If there were no OH shift, then the ionic form would be indicated. A choice between the other two formulas rests on the presence of a P=O group, since both phosphoric and phosphorous acids, when ionized, can be expressed without double bonds as

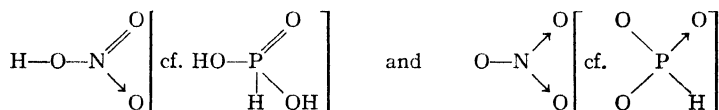


There is no actual difference between the $\text{P} \rightarrow \text{O}$ coördinate linkage and the $\text{P}=\text{O}$ linkages once the linkage is formed, so that the net result is



between the two acids on a double bond basis if these were the only forms of the acid present. The difficulty is in being able to point with certainty to which, if any, of these compounds contains the $\text{P}=\text{O}$ group.

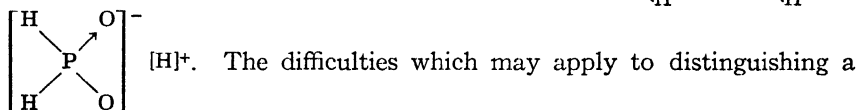
By analogy with



one would expect a strong frequency in the region between $\Delta\bar{\nu}$ 1400–1600, corresponding to the $\text{P}=\text{O}$ oscillation, or more exactly, that vibration of the whole pyramid which simulates this motion. No such frequency is present.

Hypophosphorous Acid

Hypophosphorous acid exhibits at least one if not two Raman shifts in the $\Delta\bar{\nu}$ 2400 region. This acid may be written as $\text{P} \begin{array}{l} \nearrow \text{OH} \\ \nearrow \text{OH} \\ \searrow \text{H} \end{array}$, $\text{O}=\text{P} \begin{array}{l} \nearrow \text{OH} \\ \searrow \text{H} \\ \searrow \text{H} \end{array}$ or



$\text{P}=\text{O}$ shift in phosphorous acid are present here also. Only one of the three hydrogen atoms may be replaced by a metal, thus indicating two $\text{P}-\text{H}$ linkages. In both of these acids this linkage is modified by substitution. This is shown by the following data:

H_3PO_3	KH_2PO_3	K_2HPO_3	H_2PO_3	NaH_2PO_3
2485, 2511	2396	2314	2415	2353, 2450

from which it is evident that the alkali substitution strongly influences the vibrations of the rest of the molecule. This is more attributable to hydrogen removal than to alkali addition. The amount of change is comparable to that observed with hydrogen chloride as a function of polar environment.

Selenic and Selenious Acids and their Salts

Selenic Acid.—Selenic acid is of particular interest because of its relation to the sulfur acids. Venkateswaran¹⁶²⁹ has investigated selenic and selenious acids in a comprehensive fashion. Some of these results are indicated in Table 75.

Table 75.—The Raman Shifts from Selenic Acid.

State of Substance	1	2	3	4	5	6	7	8	9	10	11	12
Crystal	327(1)	355(1)	374(2)	766(5)	778(1)	—	896(5)	—	—	930($\frac{1}{2}$)	—	1383(1)
Molten	294(3)	361(6)	388(6)	756(10)	—	—	914(8)	—	—	996(3)	1186 } ⁽⁰⁾	—
											1105 }	—
Super-cooled	294(3)	360(3)	387(3)	752(10)	—	—	899(8)	—	—	978(2)	—	—
% Selenic Acid in aqueous sol.												
92.5	299(5)	374(5)	—	747(10)	—	—	862(5)	—	927(2)	951(1)	1160(0)	—
75	307(4)	390(3)	—	748(6)	—	—	826(8)	—	934(3)	—	—	—
50	312(3)	390(3)	—	742(3)	—	845(0)	862(10)	—	929(3)	—	—	—
30	327(3)	390(3)	—	737(3)	—	846(1)	866(10)	910(0)	929(2)	—	—	—
20	332(3)	398(3)	—	732(2)	—	845(2)	866(8)	908(2)	925(2)	—	—	—
15	332(3)	400(3)	—	732(1)	—	845(4)	866(8)	908(2)	921(1)	—	—	—
7.5	332(1)	402(1)	—	732(0)	—	845(3)	866(6)	908(1)	912(0)	—	—	—

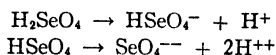
The crystalline acid has seven sharp frequencies at $\Delta\bar{\nu}$ 327(1), 355(1), 374(2), 766(5), 778(1), 896(5), and 930($\frac{1}{2}$). The relatively weak band at $\Delta\bar{\nu}$ 930 is displaced by a higher frequency $\Delta\bar{\nu}$ 996 on melting and disappears entirely on dilution below 75 per cent. A new band appears at $\Delta\bar{\nu}$ 927 at about 90-per cent acid. This becomes a doublet near 30-per cent acid, the $\Delta\bar{\nu}$ 910 component increasing in intensity with dilution and $\Delta\bar{\nu}$ 927 decreasing in intensity. The shift at $\Delta\bar{\nu}$ 845 likewise begins near 50-per cent acid and progressively increases in intensity with relative dilution (concentration $\times$ exposure = a constant).

The three lowest frequencies in the crystal are also influenced by a change of state and by dilution. One of these, $\Delta\bar{\nu}$ 374(2), disappears entirely on solution. All these changes indicated a pronounced alteration in the molecular species according to the environment. Polarization measurements¹⁶³¹ indicate that $\Delta\bar{\nu}$ 756 and 914 of the molten acid (866 in solution) are the most polarized ($\rho = 0.30$). The first of these decreases in intensity with dilution and the second increases.

It is probable therefore that they represent the symmetrical vibrations of the selenic acid molecule and the selenate ion respectively. The selenate ion, indicated by $\Delta\bar{\nu}$ 845, appears only in solutions more dilute than 50-per cent.

These assignments are probably reasonably accurate. Other assignments may be made of other frequencies with a fair degree of accuracy. For the selenic acid molecule, $\Delta\bar{\nu}$ 397 and 996 could probably be added. The two lowest lines $\Delta\bar{\nu}$ 294(3) and 361(6) are common to all the species present and behave in a fashion similar to $\Delta\bar{\nu}$ 417 and 595 which appear in sulfuric acid. The shifts $\Delta\bar{\nu}$ 845 and 908 vary in somewhat the same fashion

as $\Delta\tilde{\nu}$ 895 and 1040 in sulfuric acid. The doublet nature of the lines observed by Venkateswaran¹⁶²⁹ is similar to the composite nature of the sulfuric acid lines as observed by Woodward and Horner. The ionization process would seem to fall into the same general pattern, namely,



For KHSeO_4 $\Delta\tilde{\nu}$ 339 and 852 have been observed. The latter is in reasonable agreement with the line at $\Delta\tilde{\nu}$ 862 assigned to the HSeO_4 ion.

Ganesan⁵⁷³ somewhat earlier investigated the Raman spectra of several salts of selenic acid. The sodium, potassium, ammonium, magnesium, and thallous selenates exhibited four frequencies which varied little if any with the cation. These are $\Delta\tilde{\nu}$ 340(4), 411(4), 835(9), and 872(1). Venkateswaran's values which have been cited already are in reasonable agreement with these values as far as the dilute acid solutions are concerned. Those shifts then, that are common to the selenate ion, are capable of some degree of delincation and follow the general pattern that has been outlined previously. Among other factors this indicates the presence of some un-ionized selenic acid even in the most dilute solutions. Calculations by Ganesan on the basis of a tetrahedral molecule of the type AX_4 lead to a force constant of 4.22×10^5 dynes per cm, which is slightly less than that observed for the sulfate ion. If, instead of using the dynamic theory of vibrations as worked out by Dennison, one uses Nath's,¹¹⁶⁷ which takes into consideration a repulsive force between the two corner atoms, the force constant of the Se—O linkage becomes 5.3×10^5 dynes per centimeter.

Selenious Acid.—Although selenious acid is the counterpart of sulfurous acid, there is no resemblance in their spectra. Sulfurous acid gave the spectrum of sulfur dioxide. Selenious acid yields some thirteen lines in the crystal, according to Venkateswaran.¹⁶³⁰ In molten selenious acid, $\Delta\tilde{\nu}$ 910(3) has a depolarization factor $\rho = 0.44$ which is the most completely polarized of all the lines measured.¹⁶³¹ The polarization is surprisingly small. The lines at $\Delta\tilde{\nu}$ 862(10) (see $\Delta\tilde{\nu}$ 892 for earlier result) and 690(10) have a value of $\rho = 0.5$. The remaining lines except $\Delta\tilde{\nu}$ 545, which is polarized to an uncertain degree, are all depolarized $\rho \approx 6/7$. The observed values for the solid, liquid, and solutions are shown in Table 76.

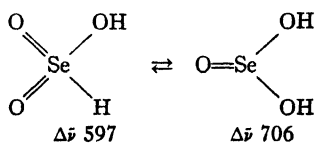
It will be seen that the lattice vibrations in the crystal, ranging from $\Delta\tilde{\nu}$ 124(1) to possibly $\Delta\tilde{\nu}$ 299(2), merge in solution into one broad band at $\Delta\tilde{\nu}$ 355(2). The group extending from $\Delta\tilde{\nu}$ 862 to 910 likewise merges into one broad line: $\Delta\tilde{\nu}$ 892 (center) 862 (maximum). It is noticeable that in the aqueous solutions there is very little change in the relative intensity of the lines with dilution. This is unlike the behavior found with sulfuric,

Table 76.—The Raman Shifts from Selenious Acid.

Solid 30° C.	Molten 70° C.	Aqueous Solutions				
		60%°	40%°	30%°	15%°	7.5%
124(1)						
199(3)						
254(6)	238(1)					
287(1)						
299(2)	343(4)	355(2)	355(2)	355(1)	355(1)	--
364(0)	380(3)					
524(3)						
	545(1)	528(0)	528(0)	528(0)	528(0)	--
597(8)						
706(3)	690(10)	695(6)	695(6)	695(6)	695(6)	695(6)
862(10)*	862(10)	865(6)	870(6)	876(6)	876(6)	880(6)
909(2)	910(3)					

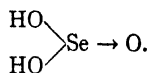
*Corrected from $\Delta\bar{\nu}$ 892 as a compromise.

nitric, phosphoric, and selenic acids. This would seem to indicate that the molecular species present in the 60-per cent solution remains without change at the more dilute concentrations. The strongest line which persists throughout all changes of state and concentration is the band whose maximum is approximately $\Delta\bar{\nu}$ 862. This must correspond to the symmetrical expansion and contraction of the SeO_3 -group. The ions HSeO_3 and SeO_3 are indicated respectively by $\Delta\bar{\nu}$ 335(1), 602(1), 862(5), and 375(1), 734(1), 806(5), 862(5) from measurements made with the sodium salts of selenious acid. In comparing these shifts with those of the acid it is noticeable that $\Delta\bar{\nu}$ 862 appears in all these compounds and in much the same position in selenic acid. One other line which appears in the solid with considerable intensity and, possibly, in methyl alcohol solution is $\Delta\bar{\nu}$ 597(8). This does not appear in the liquid or aqueous solutions. Venkateswaran^{1630, 1631} has pointed out that this shift and $\Delta\bar{\nu}$ 706 appearing in all states of the acid might correspond to the unsymmetrical and symmetrical forms of selenious acid. It is postulated that these exist in dynamic equilibrium according to the following equation:



It is concluded that in the solid both forms are present. One form predominates, however, in alcohol solution while the other predominates in the aqueous solution.

These suggestions are interesting but are not predicated on too sound a foundation. It seems that the structure of the undissociated acid is more consistent with the following:



Certainly the unsymmetrical form of the acid having the shift $\Delta\bar{\nu}$ 597, according to Venkateswaran, could be ruled out as an important possibility because of the lack of the Se—H shift. This would appear, if present, near $\Delta\bar{\nu}$ 2312. The corresponding shift does occur in phosphorous acid and is not present in sulfurous acid. From these results there seems to be little evidence for the existence of a free selenious ion in a solution of the acid. This ion has a strong frequency near $\Delta\bar{\nu}$ 806 which is completely absent in even the most dilute solutions of selenious acid. As far as the HSeO_3 ion is concerned, one can assume that it is not possible to distinguish the shifts of this ion from those of liquid selenious acid which fall in the same region. The other, more likely, interpretation is that the acid, even in the liquid state, may be partially ionized. The frequency which appears at $\Delta\bar{\nu}$ 355 is split into two components in the liquid and probably belongs to one of the fundamental vibrations of the molecule. The group of low frequencies may be, as has been stated, lattice vibrations or incomplete molecular rotations. On the other hand there may be intermolecular vibrations of the hindered translational type observed in water. It has been suggested that the extreme broadening of some of the lines is due to a tendency toward association.

The principal conclusion, as far as the investigation of selenic and selenious acid is concerned, is that selenic acid behaves in much the same fashion as sulfuric or phosphoric acid, but that selenious acid does not simulate the behavior of either sulfurous or phosphorous acid.

Chapter 25

The Raman Spectra of Some Sulfur Compounds

Sulfur Dioxide, Sulfur Trioxide and Related Compounds

The strongest shift occurring in gaseous sulfur dioxide is near $\Delta\bar{\nu}$ 1150. In the liquid this may be decreased slightly but the magnitude of the purported decrease is usually within the experimental error of the observations. However, two other frequencies appear at $\Delta\bar{\nu}$ 526(0) and 1334(1) in the liquid. All of these are practically unaffected by changes in temperature or by solution in water.⁵⁸⁷ The polarizations as indicated by the values of ρ for the three lines $\Delta\bar{\nu}$ 526, 1150 and 1334 are, respectively, 0.6, 0.14, and 0.08.³³⁰ Three Raman frequencies are to be expected from sulfur dioxide if it is a non-linear triatomic molecule. The symmetrical (ν_r or ν_1) parallel vibration corresponds to $\Delta\bar{\nu}$ 1150. The deformation vibration (δ_r or ν_2) can be assigned to $\Delta\bar{\nu}$ 526 and the ν_s or ν_3 to $\Delta\bar{\nu}$ 1334. This is unchanged on solution in dimethyl ether.¹⁶⁵¹

As the spectra of sulfur dioxide and trioxide generally have been determined together—or at least considered together—they will be so treated here. The number of frequencies to be expected from sulfur trioxide is three if the molecule corresponds to the plane form and has the symmetry D_{3h} , or four if it is pyramidal and has the symmetry C_{3v} . In both cases there will be two doubly degenerate depolarized frequencies and one symmetrical polarized one. In the pyramidal model there will be an additional polarized frequency corresponding to a symmetrical vibration. None of the actual observations, however, is in accordance with either of these views. For sulfur trioxide at room temperature there are at least nine lines, according to Bhagavantam.¹²⁴ On heating the sulfur trioxide to 100° there is a considerable diminution in the intensity of approximately six of these lines. In general these observations have been confirmed by Gerding and his co-workers.^{585, 586, 587, 589, 590} The number of frequencies found is too large to be explained by the presence of anything but polymerized molecules of the type $(SO_3)_x$. Mixtures of the dioxide and trioxide molecules result only in a diminution of the intensity of the former proportional to its concentration, whereas those which correspond to the trioxide polymer diminish quite markedly. The shifts at $\Delta\bar{\nu}$ 525, 1068, and 1403 which can be assigned to the sulfur trioxide molecule increase in intensity with temperature elevation. Of these only $\Delta\bar{\nu}$ 1068 is very strong in the gaseous

phase. The shifts which may be assigned at least provisionally to sulfur dioxide, sulfur trioxide and the polymer of sulfur trioxide are indicated in Table 77.

Table 77.—The Raman Shifts from Sulfur Dioxide, Sulfur Trioxide and Sulfur Trioxide Polymer.

SO ₂ Gaseous	SO ₂ Liquid	SO ₃ Gaseous	SO ₃ Liquid Approx. 100° C.	SO ₃ Liquid Approx. 20° C.	SO ₃ Solid Form
				166(1)	
					254($\frac{1}{2}$)
				290(6)	292(1)
				319(1)	323(0)
				370(7)	371(1)
				408(1)	410(0)
				483(1)	
	526(0)		525(2)	531(3)	525(0)
				597($\frac{1}{2}$)	578(0)
				650(2)	650
				668(3)	662($\frac{1}{2}$)
				699(3)	698($\frac{1}{2}$)
				775(0)	
				840(1)	841(0)
				866($\frac{1}{2}$)	
		1068(1)	1068(7)	1068(5)	1074($\frac{1}{2}$)
1145(3)	1150(5)			1229(1)	1230(0)
				1271(6)	1273(2)
	1334(1)				
			1395(2)	1390(1)	
				1490(2)	1483(1)
				1516(1)	

It is presumed⁵⁹⁰ that the polymeric form is S₃O₉ as the number of shifts recorded is in excess of 18, the maximum amount of fundamental shifts which may be expected of S₂O₆. Gerding and Moerman⁵⁸⁶ postulate the existence of two kinds of sulfur trioxide in the solid state, γ -SO₃ and β -SO₃. The shifts from one of these, the γ form, are included in the foregoing table. It is presumed that this form exists as a six-membered ring containing three oxygen and three sulfur atoms with a small amount of monomolecular sulfur trioxide in solid solution. The β -SO₃ is likened to asbestos and occurs as a chain with alternate single-bonded sulfur and oxygen atoms, together with double-bonded oxygen atoms attached to each sulfur atom. These interpretations of crystalline structure are to be accepted with caution at this time. On the other hand there seems to be no doubt that there is a change in the molecular constitution of sulfur trioxide with an elevation in temperature corresponding to approximately 100° C. and that this change can be attributed to a depolarization of the SO₃ polymer. This is one of the concrete examples of the utility of the Raman effect in differentiating between various molecular structures in inorganic chemistry.

In addition to this phase of the Raman shifts of sulfur dioxide and sulfur trioxide there is, of course, also the relationship between the spectra obtained from these compounds and those obtained from others containing at least a portion of these groups. The relationship is not as clear as it might be in those compounds containing an S—O linkage, as is set forth in Table 78. The lack of any great similarity between the spectra of these

Table 78.—The Raman Shifts of Some Sulfur Oxides.

Cl_2SO		Cl_2SO_2		$\text{HO}-\text{SO}_2$		$\text{HO}-\text{SO}_2$		SO_2		SO_3	
$\Delta\tilde{\nu}$	ρ	$\Delta\tilde{\nu}$	ρ	$\Delta\tilde{\nu}$	$\Delta\tilde{\nu}$	ρ	$\Delta\tilde{\nu}$	ρ	$\Delta\tilde{\nu}$	ρ	$\Delta\tilde{\nu}$
192(5)	0.45	214(5)	0.7								
282(5)	6/7	280(2)	6/7								
				312(3)							
343(8)	0.15	365(1)	6/7								
		395(5)	6/7								
		408(10)	0.07	419(4)	390(2)	6/7					
443(5)	6/7				410(2)	6/7					
488(4)	0.08			485(0)							
				513(1)							
		560(5)	0.06	564(0)	560(3)			526(0)	0.6		525(2)
		576(0)	6/7								
				623(6)							
				724(0)	(740)						
				812(0)							
				919(4)	910(8)	0.16					
					980(1)	0.03					1068(7)
				1155(3)	1120(2)						
1229(3)	0.13	1190(1)	0.2	1199(2)	1170(2)			1150(5)	0.14		
		1415(0)	6/7	1400(2)	1360(1)			1334(1)	0.8		1395(2)

compounds is due not only to the increased mass resulting from chlorine substitution but also to a change in molecular configuration. The vibrations of either a tetrahedral or pyramidal molecule are for the most part different from those of a plane molecule. The mechanism used to assign some specific vibrations to the valence oscillations does not lead to so fruitful a result as was possible in dealing with organic compounds. The question of interpretation is complicated further by a process of partial ionization in at least two of the compounds. Nevertheless, it is obvious that the Raman shifts below $\Delta\tilde{\nu}$ 400 involve the chlorine oscillation. It is apparent also that the shifts near $\Delta\tilde{\nu}$ 1200 are concerned with the S—O vibration. From the value of the polarization it is a reasonable presumption that this may correspond to the characteristic valence vibration. Nisi¹¹⁷⁸ draws attention to the fact that there is no Raman shift at $\Delta\tilde{\nu}$ 1200 in sulfur monochloride.

According to Venkateswaran,¹⁶¹⁶ Cabannes and Rousset³⁸⁰ and Matossi and Aderhold¹⁰³⁹ the structure of thionyl chloride is $\text{Cl}_2\text{S}=\text{O}$. The molecule is considered by Cabannes and Rousset to have a pyramidal configuration

and gives rise to six observed Raman frequencies. The $\Delta\bar{\nu}$ 193 is presumed to occur when the SO-group oscillates as a unit against the two chlorine atoms, which in turn vibrate along the lines of the binding force against the SO-group. The frequency at $\Delta\bar{\nu}$ 488 occurs when the sulfur atom remains fixed and the chlorine and oxygen atoms vibrate symmetrically. When the two chlorine atoms remain fixed and the oxygen and sulfur oscillate against each other, the shift at $\Delta\bar{\nu}$ 1229 is obtained. The presence of six frequencies in place of the usual four obtained from a pyramidal molecule is no doubt due to the lack of symmetry in the thionyl chloride molecule. This causes a splitting of the two degenerate vibrations into two components each. In accordance with this view, three of the lines are depolarized. Unfortunately, however, one of the three lines is considerably polarized, having a value of the depolarization constant of 0.15. Thionyl fluoride likewise has six lines, namely, $\Delta\bar{\nu}$ 326(1), 395(6), 529(8), 720(9), 795(9) and 1312(10) according to Yost (Raman Jubilee volume).

Sulfur monochloride has the formula S_2Cl_2 , and is the polymerized form of SCl . The principal shifts of this compound are 109(5), 206(4), 247(2), 447(10) and possibly 536. The existence of these frequencies demonstrates that the compound cannot be, in liquid form, diatomic, that is, SCl . The structure of this compound may be written in two ways, $S=SCl_2$ or $Cl-S-S-Cl$. The first of these formulas would have six fundamental Raman frequencies, three polarized and three depolarized, according to a molecule with the symmetry D_{2v} . The second postulated formula corresponds to a molecule with the symmetry $D_{\infty h}$ and should give rise to three Raman frequencies, two polarized and one depolarized and doubly degenerate. In view of the fact that the intensity measurements of the observed frequencies of sulfur monochloride are at best mediocre, and considering also the lack of any polarization data, it becomes more a matter of speculation than of weighed opinion in deciding between the applicability of these formulas. However, it would seem that the linear $Cl-S-S-Cl$ formula is the more probable. The additional line, that is the one or possibly two in excess of the expected three, may be accounted for on the basis of a harmonic. Within the accuracy of these observations it can be seen that $\Delta\bar{\nu}$ 206 is a multiple of 109. Free rotation around the $S-S$ bond is advocated by Morino and Mizushima.¹¹³⁸

There is another line of reasoning that would seem to substantiate the linear molecule containing single-bonded sulfur. In Chapter 17 it was seen that there is a fairly characteristic Raman shift, corresponding to the $S-S$ vibration, which occurs between $\Delta\bar{\nu}$ 487 and 508. In the more complicated derivatives this occurs almost uniformly near $\Delta\bar{\nu}$ 486. The only frequency which occurs in sulfur monochloride near this value is the one

appearing at $\Delta\bar{\nu}$ 447. This could be reasonably ascribed to the $S \leftrightarrow S$ vibration, diminished somewhat by the proximity of the chlorine atom. In any case if the $S=S$ group were present, the frequency which should correspond to this type of binding would occur near $\Delta\bar{\nu}$ 780, assuming $\Delta\bar{\nu}$ 480 was characteristic of the single-bonded sulfur linkage. As no such frequency appears, this seems to be evidence against the presence of any double-bonded sulfur and hence against the type of formula including this structure. Matossi and Aderhold¹⁰³⁹ and Meyer¹⁰⁹¹ both maintain that the structure of sulfur monochloride is similar to that of thionyl chloride. The accumulation of data since these views were expressed provides evidence against them and they may be considered obsolete now.

Sulfites and Complex Sulfur Compounds

The simplest compound involving sulfur as an ion is sulfurous acid. This compound was discussed under the Raman spectra of the acids. It was concluded that sulfurous acid, as such, must exist only in low concentration and that the larger portion of the sulfur is in the form of sulfur dioxide dissolved in water.

The sulfites and the acid sulfites should present some illuminating information in regard to the configuration of the sulfite ion and its relation to sulfur dioxide. Unfortunately most of the work on these compounds was done quite a number of years ago when the technique of obtaining Raman spectra was still wrapped in its swaddling clothes. Since that time both accuracy of making measurements and technique have improved. While many observations and measurements made during this period have stood the test of repeated reexamination, it is felt that the sulfites should be reexamined before too much weight is placed upon the conclusions based on the early experimental work.

The initial attempts to determine the Raman spectrum of the sulfite ion led only to the detection of the relatively strong line¹¹⁷⁵ at $\Delta\bar{\nu}$ 968. This is appreciably lower than that observed by Dickinson and Dillon⁴⁸² at $\Delta\bar{\nu}$ 988. Fadda⁵⁴⁰ assigned $\Delta\bar{\nu}$ 471, 602, and 984 to the sulfite group. These lines are so close to those observed in sulfate solutions that this appears more than a coincidence. The existence of the HSO_3^- ion is subject to some dispute. Ghosh and Das⁵⁹⁸ have recorded $\Delta\bar{\nu}$ 346, 826, 963, and 1406 for this ion in the solution of sodium hydrogen sulfite. The assignment by Nisi¹¹⁷⁸ of $\Delta\bar{\nu}$ 1054 and by Fadda of $\Delta\bar{\nu}$ 1199 to this ion is probably erroneous. More recently it has been the contention of Fadda⁵⁴¹ that $NaHSO_3$ does not exist in solution. The spectrum obtained from this compound indicates only the presence of $S_2O_5^{2-}$ ions according to a possible equilibrium $2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$. Fadda observed for a solution of sodium hydrogen sulfite $\Delta\bar{\nu}$ 242(6), 420(4), 656(5), and 1009(7). These

values are reasonably close to those observed by Nisi from a solution of sodium pyrosulfite, with the exception of $\Delta\bar{\nu}$ 571 and 1054 which were additional frequencies noted by him. These frequencies possibly are present in potassium hydrogen sulfate. It is Fadda's contention that they owe their origin to a slight oxidation in the solutions employed by Nisi. This was confirmed by repeating the experiment in the absence of air. Under these conditions these two lines were not observable. This leaves then reasonably good agreement between the Raman spectrum of sodium pyrosulfite (as determined by Nisi but omitting $\Delta\bar{\nu}$ 571 and 1054) and the supposed sodium hydrogen sulfite solutions as determined by Fadda. The logical conclusion from these experiments is to uphold the contention that the equilibrium is in the direction of the production of S_2O_6 ions.

However, there are some factors of uncertainty in these experiments for, if $\Delta\bar{\nu}$ 1054 is to be attributed to atmospheric oxidation of Nisi's solutions, a large per cent of the salt must have been oxidized. The appearance of $\Delta\bar{\nu}$ 314 in a solution approximating 50-per cent may be ascribed to the presence of a polymer of sodium pyrosulfite, but the evidence is rather inadequate. In any case there is nearly complete disagreement between these results and those of Ghosh and Das already referred to.

The next more complicated compound in this series is sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$. The sulfates, which could be considered here, will be discussed separately since they constitute such a large group. The similarity between the spectrum of sodium thiosulfate and that of the sulfates is marked. This is most reasonably explicable on the assumption that the S_2O_3 ion has a constitution similar to the sulfates, that is, with one oxygen replaced by a sulfur atom and the other oxygen atoms being bound to one sulfur atom only. These results may be compared with the shifts observed by Nisi ¹¹⁷⁹ for crystalline $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. These are $\Delta\bar{\nu}$ 324, 433(s), 546, 612, 674, 1018, 1116, and 1162. With allowance for possible lattice frequencies and the tendency to split frequencies in crystals, the results are reasonably compatible with those obtained from solutions. Each of the lines, corresponding to the two active vibrations, clearly splits into more than one component. The relative intensities, however, of the inactive vibrations for S_2O_3 are the reverse of those which exist in the case of the sulfates.

According to Pringsheim and Yost,¹²⁵⁹ in the S_2O_6 ion the oxygen atoms are symmetrically arranged with respect to each sulfur atom, giving the formula $\text{O}_3\text{S}-\text{SO}_3$. It may be mentioned again that the characteristic frequency of the $\text{S} \leftrightarrow \text{S}$ vibration in the organic disulfides, such as methyl disulfide, occurs ¹⁶¹⁵ at $\Delta\bar{\nu}$ 512. There is no counterpart for this in the S_2O_6 ion.

The compound $\text{Na}_2\text{S}_2\text{O}_4$, sodium hyposulfite, can be equally well written

NaSO_2 . In the presence of water only slightly above room temperature it may be converted into $\text{Na}_2\text{S}_2\text{O}_3$ and NaHSO_3 . The Raman spectrum is not consistent with the formula NaSO_2 since the dissociation of this compound would lead to a spectrum more similar to that of sulfur dioxide than the one observed. From the analogy of the spectrum with that of the sulfates, it might be presumed that the oxygens are attached to one rather than to both sulfur atoms.

The compound $\text{K}_2\text{S}_2\text{O}_7$, potassium pyrosulfate, in solution gives, according to Nisi,¹¹⁷⁵ a Raman spectrum which nearly coincides with that given by potassium hydrogen sulfate, KHSO_4 . This is not surprising when one considers that the pyrosulfate is obtained by dehydrating two molecules of the acid sulfate, and probably results, on solution, in the formation of HSO_4 ions. It will be remembered that pyrosulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$, in sulfuric acid solution yielded $\Delta\tilde{\nu}$ 300(1), 327(5), 480(3), 735(5), 960(3), 1250(8).

Sulfates

The sulfates were among the earliest inorganic compounds investigated. It is generally conceded that these compounds have a tetrahedral symmetry, T_d , in which there are nine fundamental oscillations, four of which appear in Raman spectra. Two of these are triply degenerate, one is doubly degenerate, and one is symmetrical and polarized. This model is similar to the one already discussed under carbon tetrachloride.

In general the four fundamental frequencies may be considered as $\Delta\tilde{\nu}$ 450, 620, 980, and 1100. There are, however, some important modifications in these frequencies depending on the state of aggregation and the cation present. Of these frequencies the one at $\Delta\tilde{\nu}$ 980 is the strongest and certainly corresponds to the symmetrical oscillation of the tetrahedron. These results are summarized in Table 79 which, as in the case of the nitrates, represents an average value for these shifts. This averaging method has been adopted because the errors in the work of different investigators are of the same magnitude as the minor variations in frequency due to other influences. It is felt that it would be better to consider small but important variations separately. These small alterations should be evaluated from work done under comparable conditions.

It was originally believed from the work of Embirikos⁵²⁹ that the magnitude of some of the shifts of the sulfate ion was influenced by concentration. These observations, however, have been questioned. Coon and Laird³⁸² have investigated magnesium sulfate and have come to the conclusion that any change in the Raman shifts with concentration is probably less than two wave numbers. Mitra,¹¹¹¹ who investigated magnesium and lithium sulfates up to a concentration amounting to five

Table 79.—The Raman Shifts from Some Sulfates.

Compound	Raman Shifts									
	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}
Li ₂ SO ₄	440(1)	595(1)			997(3)			1104(1)		
LiKSO ₄					1010(3)			1110(1)		
Na ₂ SO ₄	460(3)	615(1)			990(6)			1115(1)		
KHSO ₄	427(1)	593(1)			980(2)			1050(5)		
K ₂ SO ₄	454(1)	617(1)			986(6)			1090(0)		
Rb ₂ SO ₄	453(1)				976(3)					
(NH ₄) ₂ SO ₄	453(2)	616(1)			977(4)			1053(1)		
BeSO ₄	450(2)	620(1)			990(4)			1108(1)		
CuSO ₄	448(3)	471(3)	589(0)		983(4)			1108(1)		1143(1)
MgSO ₄	456(2)	613(1)			985(4)			1063(0)		1476(0)
CaSO ₄ (Anhydrite)	415(3)	499(3)			1013(8)			1108(1)		1160(2)
CaSO ₄ (Gypsum)	415(5)	492(3)								
SrSO ₄	460(3)	620(1)	671(2)		1005(8)			1113(1)		1135(5)
BaSO ₄		628(0)			999(6)			1106(2)		
	62(0)	74(1)	88(0)	98($\frac{1}{2}$)				1110(1)		
ZnSO ₄	127($\frac{1}{2}$)	150(1)	190(1)							1160(1)
CaSO ₄ · 8/3H ₂ O	224(0)	340(1)			625(1)—649(2)			1104(1)		
HgSO ₄	450(1)				989(10)			1108(0)		
Al ₂ (SO ₄) ₃	462(2)				980(4)			1088(1)		
KAl(SO ₄) ₂	499(2)	621(2)			1010(8)			1042(4)		
PbSO ₄	457(2)				986(4)			981(6)		1327(3)?
	461(1)	527(1)			984(3)			1088(1)		
MnSO ₄		600(1)						1062(3)		
FeSO ₄	448(0)	668(3)			990(4)			1086(0)		
FeNH ₄ (SO ₄) ₂		606(0)			978(2)			1096(0)		
NiSO ₄	3817	673			992(3)					
UO ₂ SO ₄	460(0)	620(2)			980(3)					1120(2)
					(870)					

*No ammonium ion shifts are included in this table.

molal, believes that there is relatively no frequency change in solution as a function of concentration. Simon ^{144b} finds constant values for sulfate ions in solution.

In contrast to the negligible influence of concentration, a change of state from solid to solution does cause diminutions in $\Delta\bar{\nu}$ 450, 620, and 980, amounting to between two and 20 wave numbers. In addition to this effect it has been indicated by Krishnamurti ⁹⁰⁸ that the strongest sulfate shift near $\Delta\bar{\nu}$ 1000 decreases in the crystals with increasing volume of the cation. With sodium, potassium, and ammonium sulfates, for example, this shift is respectively $\Delta\bar{\nu}$ 990, 985, and 977, while for the equivalent calcium, strontium, and barium salts it is $\Delta\bar{\nu}$ 1005, 999, and 989, respectively. In solution this effect is either absent or beyond the experimental accuracy.

It is to be noticed that the number of frequency shifts which appear far exceeds the number of possible fundamentals. The group appearing below $\Delta\bar{\nu}$ 450 have been termed lattice vibrations and are ascribed to the movement of the crystal lattice; or they may owe their origin to the motion of molecules with insufficient energy to make a complete rotation and which consequently oscillate about a mean point. The few molecules which exhibit frequencies in this region are confined to those having large cations, but not all molecules with large cations exhibit low-frequency Raman shifts, although this may be due to an insufficient exposure. The compounds which have been most carefully investigated are those which commonly occur in crystals of reasonable size. The lack of frequencies in the region between $\Delta\bar{\nu}$ 980 and 1150 may also be due to the lack of observation rather than to a genuine absence. There is no doubt about the occurrence of multiple frequencies in this region. Furthermore the number of lines which appear depends on the state of aggregation. In cadmium sulfate hydrate, for example, there are at least four frequencies in excess of $\Delta\bar{\nu}$ 600. The shift at $\Delta\bar{\nu}$ 1110 in the solution is very broad and diffuse but in the hydrated molecule it is split into strong and sharp components. This tendency has also been noted in anhydrite and gypsum by Bhagavantam (Raman Jubilee volume). The frequency which appears near $\Delta\bar{\nu}$ 1070 might be a combination of the ones at $\Delta\bar{\nu}$ 450 and 610; or some of the frequencies might be the result of a coupling between these two frequencies of the type which occurs in carbon dioxide. The intensity relations, however, do not seem to favor either of these hypotheses in all cases. It would seem more likely that the appearance of some of these frequencies can be attributed to a decrease in the symmetry of the tetrahedron as a result of the influence of the cation or of the water of crystallization, with a consequent appearance of new lines for those frequencies which were doubly or triply degenerate in the more symmetrical molecules.

This is shown clearly in Figure 68 which depicts these changes by means of microphotometer tracings. The solutions of zinc, nickel and beryllium sulfate hydrate yield a spectrum which is noticeably different. The broad band at the left of each picture is the exciting band and the band at the

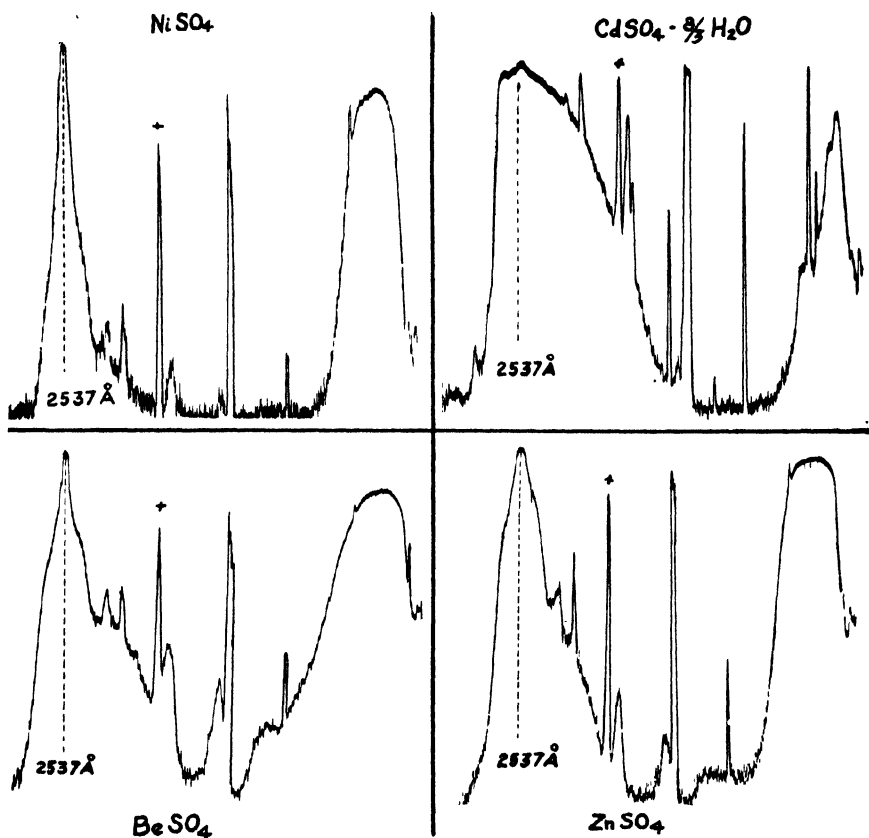


FIGURE 68. Microphotometer Tracings of the Raman Spectra of Some Sulfates Showing the Splitting of the $\Delta\bar{\nu}$ 1050-1110 Shifts as a Result of Crystal Formation.

right is from water of crystallization or liquid water. The line marked with a cross is the shift at approximately $\Delta\bar{\nu}$ 980. To its left are the two weak lines which correspond to the ν_2 (doubly degenerate) and ν_4 (triply degenerate) vibrations, and to the right the line or lines due to the triply degenerate, ν_3 , unsymmetrical vibration.

Acid Sulfates

The HSO_4 ion is mentioned under the discussion of sulfuric acid. The principal shift appears near $\Delta\tilde{\nu}$ 1045. Padda⁵⁴⁰ records for potassium hydrogen sulfate $\Delta\tilde{\nu}$ 427, 593, 978, and 1047. Bernstein, Romans, Howden, and Martin¹¹⁹ observe for sodium hydrogen sulfate $\Delta\tilde{\nu}$ 420, 580, and 1050, and Shaffer and Cameron¹⁴²³ find $\Delta\tilde{\nu}$ 436, 599, 906, 975, and 1040 for a 34-per cent solution. The last two authors attribute $\Delta\tilde{\nu}$ 906 and 1040 to the HSO_4 ion and the remaining shifts to the sulfate ion. These authors note both a change in frequency of some of the shifts with dilution and also a change in intensity (the absolute intensity being compensated for dilution). In a 13-per cent solution the shifts are $\Delta\tilde{\nu}$ 438, 611, 917, 978, and 1958. This may account for the discordant values found by different observers. The intensity changes have been used to estimate the relative degree of dissociation of potassium hydrogen sulfate. If a 13-per cent solution is arbitrarily assumed to be 100-per cent dissociated, a 35-per cent solution is found to be 60-per cent. There are no lines corresponding to the influence of the potassium ion.

It would seem that the acid sulfates dissociate progressively in a fashion similar to sulfuric acid. On the other hand, some of the shifts remain relatively constant so that the general characteristics of the acid sulfates represent a compromise between the behavior of the sulfate ion and the acid.

Carbon Disulfide

Two frequencies are observed for carbon disulfide, namely, $\Delta\tilde{\nu}$ 655 and 796. The presence of but two frequencies is reminiscent of the spectrum of carbon dioxide, and, as a matter of fact, carbon disulfide is supposed to have the same molecular configuration as carbon dioxide. The infrared absorption of this molecule indicates the presence of a frequency at $\Delta\tilde{\nu}$ 397 and one at $\Delta\tilde{\nu}$ 1523, both of which are doubly degenerate. These, together with the two Raman active frequencies, provide the necessary four lines if one is to be considered a harmonic of another. If the ν_2 or perpendicular bending type of oscillation is ascribed to $\Delta\tilde{\nu}$ 397, then it can be seen readily that $\Delta\tilde{\nu}$ 795 corresponds to $2\nu_2$. This leaves $\Delta\tilde{\nu}$ 655 as the ν_1 type of oscillation corresponding to the valence vibration $\Delta\tilde{\nu}$ 1523, observed in the infrared, as the asymmetrical vibration.

Before proceeding further with a discussion of the constitution of carbon disulfide, it will be advisable to restate some of the remarks made previously in connection with some other sulfur compounds. It is indicated in the discussion of the thiocyanate ion that the S—C frequency falls near $\Delta\tilde{\nu}$ 750, while in the mercaptans and thioethers a doublet frequency

occurs at $\Delta\tilde{\nu}$ 650 and 730. In carbon oxysulfide the ν_1 vibration is $\Delta\tilde{\nu}$ 859. If it is accepted that the C—S vibration for single-bonded sulfur is in the neighborhood of $\Delta\tilde{\nu}$ 650 to 700, the interpretation of the spectrum observed from carbon oxysulfide is found to be consistent with the assumption that there is a double bond between the sulfur and the carbon atom. In this case it is postulated that the normal double-bond vibration frequency is lowered because of the so-called allenic type of linkage, the shift at $\Delta\tilde{\nu}$ 859 representing, therefore, a reduced normal double-bond shift. The S=C shift would normally appear near $\Delta\tilde{\nu}$ 1050 as estimated from the empirical relation: $\Delta\tilde{\nu}_{\text{single bond}} \times 1.6 = \Delta\tilde{\nu}_{\text{double bond}}$. In the case of carbon disulfide, however, the observed ν_1 vibration falls near the expected frequency for a single bond. This leaves one in a dilemma. Apparently the S—C shift in carbon disulfide is one which, from the Raman spectra point of view, would correspond to a single bond. It can be argued, of course, that the diminution because of the allenic type of structure would cause the possible S=C frequency in carbon disulfide to have a low value ($\Delta\tilde{\nu}$ 655); but, compared with the value obtained from carbon oxysulfide, this appears to be much too low. This explanation, therefore, seems to stretch a point beyond a degree of reasonableness. From thiophosgene (CSCl_2) Thompson has obtained some seven Raman lines, the two strongest ones being $\Delta\tilde{\nu}$ 496(5) and 1121(10). The symmetrical valence vibration is assigned to the latter shift.

On considering some of these observations more in detail, it may be remarked that Krishnamurti⁹⁰⁶ observed that the stronger of the two principal bands has a weak component at $\Delta\tilde{\nu}$ 647. This has been confirmed by Bhagavantam¹⁵⁴ and Mesnage¹⁰⁸⁷ who used spectrographs of high dispersion, thus resolving the $\Delta\tilde{\nu}$ 800 band into one component at $\Delta\tilde{\nu}$ 796 and a weaker component at $\Delta\tilde{\nu}$ 810. In general it is conceded that the ratio of the intensities of $\Delta\tilde{\nu}$ 655 to 796 are in the ratio of three to one. However Imanishi⁷⁷⁶ obtained $\Delta\tilde{\nu}$ 655 from gaseous carbon disulfide, but could not observe the shift at $\Delta\tilde{\nu}$ 796. This would indicate, if his observations are correct, that in the gaseous phase this relative intensity ratio is modified. In addition to the two principal bands so far enumerated, Bhagavantam^{123, 125, 135, 154} has observed three feeble bands at $\Delta\tilde{\nu}$ 400, 1229 and 1577, of which the one at 400 has been confirmed by Venkateswaran¹⁶¹⁹ who has also determined its polarization. By means of high dispersion Langseth, Sorensen and Nielsen⁹⁶⁶ have resolved the frequencies previously referred to into several components. These are $\Delta\tilde{\nu}$ 383, 395 (< 1) ($\rho = 0.8$) where ρ was determined by Venkateswaran,¹⁶¹⁹ and $\Delta\tilde{\nu}$ 641, 648(2), 656(10) ($\rho = 0.15$), and finally $\Delta\tilde{\nu}$ 788, 796(1) ($\rho = 0.18$), $\Delta\tilde{\nu}$ 805, and $\Delta\tilde{\nu}$ 816. A small discrepancy of a few wave numbers between these observers and previous investigators is without significance, because the usual accuracy

in reporting wave number shifts is *usually* not greater than ± 5 or 10 wave numbers. What is more important, however, is that these authors were unable to confirm the lines at $\Delta\bar{\nu}$ 1229 and 1577 reported by Bhagavantam. The satellites which give rise to $\Delta\bar{\nu}$ 648 and 805 are due to transitions similar to those giving rise to the principal bands, the only difference being that the scattering molecules are in the excited state rather than in the lower state of energy. (By excited state in this case is meant the 010 state.) It is believed by these authors, in agreement with the precepts heretofore mentioned, that a linear symmetrical triatomic molecule will have in general only one strong Raman band. The presence of two nearly equally intense bands in the Raman spectra of carbon dioxide was explained by Fermi and is a result of an abnormally large perturbation arising from the approximate coincidence of the frequency corresponding to ν_1 with $2\nu_2$. This type of accidental degeneracy probably occurs also in carbon disulfide. The polarization measurements confirm to some degree the interpretation that $\Delta\bar{\nu}$ 655 corresponds to the oscillation ν_1 or the symmetrical valence vibration. An interpretation of the satellites of these lines, however, is not possible until a more complete knowledge of the vibrational levels of the carbon disulfide molecule is obtained. It may be mentioned that Sirkar has determined the intensity of the anti-Stokes lines as compared with the Stokes lines of carbon disulfide as well as the influence of absorption on this intensity ratio.¹⁴⁵⁹ He has also observed¹⁴⁶⁹ the spectrum from solid carbon disulfide and finds that the satellite $\Delta\bar{\nu}$ 648 of the principal Raman line at 653 is totally absent at liquid air temperatures. The satellite of $\Delta\bar{\nu}$ 796, which appears near $\Delta\bar{\nu}$ 816, disappears also. The new lines, $\Delta\bar{\nu}$ 70(6) and 81(1), are present only in the solid state and are attributed to polymerized carbon disulfide rather than to lattice vibrations. It would seem more probable that the latter explanation should be accepted.

Bhagavantam and A. V. Rao¹⁶⁹ have investigated the distribution of intensity of the wings of the Raman lines observed in carbon disulfide. These do not diminish in intensity in the fashion observed for the rotational lines on each side of the Q branch, but the maximum corresponds to the center of the line. A. V. Rao¹²⁹² has investigated the spectrum of carbon disulfide with particular reference to the intensity and polarization characteristics of the Raman lines. The results which arise from this investigation are a recognition of the fact that, whereas the principal peak (referring to the microphotometer tracing of the plate) and its satellites are attributed to changes only of the vibrational energy of the molecule, the continuous spectrum on either side of these peaks has not such a simple origin. This investigation indicates that the depolarization increases with diminishing wave lengths of the exciting radiation. In general the results are in good agreement with those of Langseth, Sorensen and Nielsen

referred to previously. It is found, however, that the Q branch of the principal vibration line $\Delta\bar{\nu}$ 656 cannot be separated from the PP and the RR branches.

From the purely empirical approach as a method of determining the structure of molecules from the standpoint of Raman spectra, it has been repeatedly emphasized that in a molecule of this type the ν_1 vibration generally approaches that corresponding to the valence oscillation. Within a reasonable degree of variation this has been found to describe various types of oscillation corresponding to types of binding, such as single bonds, double bonds and triple bonds. With carbon disulfide a certain amount of uncertainty is introduced in interpreting either the structure or the spectra.

The simplest process which can be adopted to explain away any divergence is to attribute such departures to resonance vibrations, or resonance between one form of a molecule and another. While such resonance undoubtedly exists in some cases, as a general explanation it should be accepted with caution. Resonance in the carbon disulfide molecule would result in a decrease in the average force constant if the double-bond model is accepted.

All things considered, it would seem to be more reasonable to interpret the Raman spectra results as indicating a single bond between the sulfur and the carbon atom in carbon disulfide. The inconsistency of this view with the generally accepted formula is recognized. This represents one of the few anomalies in the interpretation of molecular configuration from the Raman spectra point of view.

It should be mentioned that the electron diffraction data of dimethyl sulfide indicates a C—S distance of 1.82 Å, as compared with 1.54 Å in carbon disulfide. This seems to support the C=S conception. However, if there was resonance between a single-bonded sulfur and a double-bonded one such as to produce a charged sulfur atom, the atomic distance might be more affected than the force between the atoms. Furthermore, the single-bonded sulfur distance rests on a single determination.

Chapter 26

The Raman Spectra of Silicon Compounds

Hydrogen and Halogen Derivatives

The simplest of these compounds is silane, which is the inorganic counterpart of methane. It would seem reasonable to assume that this compound has a tetrahedral symmetry of the type T_d . As is noted in the case of carbon tetrachloride, titanium tetrachloride and other similar compounds, this should give rise to four Raman frequencies, one of which is polarized and three depolarized, and of which two are triply degenerate and one doubly degenerate. In other words, there are nine fundamental frequencies which are reduced to four separate ones, unless some other factor intervenes to upset the symmetry. This would cause the degenerate frequencies to appear not as a single line, but as more than one line.

This type of symmetry description has been repeated in most of the simple compounds studied for the sake of clarifying, in each case, all the factors involved. In the case of the molecules of the type AX_3 , the convention adopted was to express the high and low parallel vibrations (or those which resulted in a change of electric moment parallel to the figure axis) as ν_1 and ν_3 , and the high and low frequencies perpendicular to the figure axis as ν_2 and ν_4 respectively. In discussing the results obtained from silane by Stitt and Yost¹⁵⁰⁷ the convention will be adopted that ν_1 represents the completely symmetrical vibration frequency, ν_2 the symmetrical twofold degenerate frequency, and ν_3 and ν_4 the high and low threefold degenerate frequencies.

From this point of view in silane ν_1 corresponds to $\Delta\bar{\nu}$ 2187, and ν_2 to $\Delta\bar{\nu}$ 978, which leaves ν_3 as $\Delta\bar{\nu}$ 2183 and ν_4 as $\Delta\bar{\nu}$ 910. The last two frequencies have not been observed in the Raman effect but are observed in infrared absorption. On this basis all of the Raman lines and the infrared absorption bands are accounted for as either harmonics of one of the fundamental frequencies or as combinations of frequencies.

However, the foregoing assignment of some frequencies does not seem to be the happiest of choices. With a halogen atom representing X in the molecule AX_4 the order of magnitude of the Raman shifts from low to high follows the general scheme $\nu_2, \nu_4, \nu_1, \nu_3$. This is independent of the mass of atom A from carbon to tin or greater. But if the atoms represented by X are light, *i. e.*, hydrogen, as in methane, or in the ammonium ion, the

order of frequencies is $\nu_4, \nu_2, \nu_1, \nu_3$. This would indicate that in silane ν_3 is $\Delta\tilde{\nu}$ 2187 and ν_1 is $\Delta\tilde{\nu}$ 2183. It is characteristic in any case that ν_1 and ν_3 lie close together and that ν_2 and ν_4 are relegated to a separate portion of the spectrum.

Silicon tetrafluoride may appropriately be considered next. The only line observed in this compound is $\Delta\tilde{\nu}$ 800 found by Yost, Lassettre and Gross.¹⁷⁴⁹ From mass considerations alone this value does not agree with the one which would be calculated for it. The same may be said also for the value of $\Delta\tilde{\nu}$ 649 observed by Suirkin and Volkenstein.¹⁶¹⁵ Neither of these results is complete; in both cases there is a change in the force constant as the result of fluorine substitution. (See Table for latest results of Yost.)

With disilane,¹⁵⁰⁸ which is analogous to ethane, there is the appearance of a line at $\Delta\tilde{\nu}$ 435 which presumably corresponds to the Si—Si vibration. Of the hydrogen oscillations, only one very strong line is observed near $\Delta\tilde{\nu}$ 2163 which is reasonably similar to that observed in silane. From an analogy with ethylene this is certainly not the only hydrogen line which should be present. From the results recorded in Table 80 may be estimated the relative force constant in the silicon compounds as compared with similar carbon compounds, and thus indirectly the binding force for these types of linkages. It will be remembered that the equation for a simple harmonic oscillator leads to the following relationships

$$\Delta\tilde{\nu}_1 = \Delta\tilde{\nu}_2 \sqrt{\frac{\mu_2}{\mu_1}} \cdot \sqrt{\frac{k_1}{k_2}}$$

from which either the expected Raman shifts may be calculated or the force constants evaluated. This equation represents, of course, only a first approximation, but it might be mentioned that the validity of other equations of this general type has been postulated on the accuracy by which results may be predicted.

Consider, for example, chloroform and chloroform-d. If the vibrating entities are considered to be a single carbon atom and a hydrogen atom or a deuterium atom, so that the vibration would be represented by $C \leftrightarrow H$ or $C \leftrightarrow D$, then, if there were no change in the force constant, the expected frequencies could be calculated by the relationship given above. The observed hydrogen-to-carbon oscillation in one case is $\Delta\tilde{\nu}$ 3016 and in the deuterium compounds $\Delta\tilde{\nu}$ 2256. The ratio of the reduced masses is 1.85 and the square root of this value is 1.36 which, on substituting in the equation just mentioned, leads to a calculated value of $\Delta\tilde{\nu}$ 3008 for the C—H frequency. This is only eight wave numbers from the observed one and is as accurate an agreement as is given by any formula so far proposed. With

silicochloroform and silicochloroform-d the square root of the reduced mass ratio yields a value of 1.39 as the proportionality factor. Substituting this value in the same equation would give a calculated Si—H frequency of 2290 wave numbers, assuming that 1647 was the correct Raman shift for the Si—D vibration in silicochloroform-d. This is a disparity of 40 wave numbers and would indicate that the force constant for the Si—H vibration is approximately three per cent lower than the equivalent Si—D force constant. This does not, however, take into consideration the experimental error involved in determining the Raman frequency shift for these two compounds. Repeated observations by different workers might reveal results which would lead to force constant values that are more nearly alike. In any case, as has been pointed out elsewhere, the calculated results agree reasonably well with the observed ones when the harmonic oscillator formula is used. This does not incorporate a number of constants which would tend to make a closer agreement between the observed and calculated values.

The application of this same procedure in comparing the force constant for Si—H in silicochloroform with C—H in chloroform leads to the result that the force constant in chloroform has nearly 1.7 times the value observed in silicochloroform; compare $\Delta\bar{\nu}$ 2914 observed in methane with $\Delta\bar{\nu}$ 2175 in silane. On applying this same line of reasoning to the Si—Cl linkage in silicochloroform, it is found that the necessary proportionality factor to convert the observed Si—Cl frequency to one corresponding to a C—Cl frequency would be 1.3, if there were no change in the force constant and if the mass effect alone were in operation.

In compounds of the type of carbon tetrachloride whose constitution is represented by a regular tetrahedron, the largest Raman frequency shift is usually the most sensitive to substitution by different cations. This shift is not ordinarily the strongest one and is completely depolarized. This occurs at $\Delta\bar{\nu}$ 615 in silicon tetrachloride. Multiplication of this by the mass correction factor 1.3 gives $\Delta\bar{\nu}$ 800 as the calculated value of the corresponding shift in carbon tetrachloride. In this compound the frequency actually appears at 780. This inevitably leads to the conclusion that the force constant in silicon tetrachloride is slightly greater than that in carbon tetrachloride as far as the Si—Cl and C—Cl linkages are concerned. In other words there is no proportionality factor representing a change in force in this case, although it has been noted already that the Si—H and C—H linkages differ by a factor of 1.7 when due allowance has been made for the change in mass. The situation is not altered by using other frequencies than the one adopted, *i. e.*, $\Delta\bar{\nu}$ 615, to make the comparison. It should be remembered that silicochloroform has a different symmetry from silicon tetrachloride, the symmetry being C_{3v} instead of T_d .

In the oscillations of the silicochloroform molecule there is one in which the hydrogen atom oscillates against the silicon atom virtually independently of the rest of the molecule. Unless such a type of motion exists, the simple harmonic method of calculating the force constant is entirely inadequate. It is not intended to overemphasize the simple method of calculation given above, but only to indicate that it has a certain utility at times.

It can be seen in the table of silicon compounds that silicochloroform and possibly trichlorobromosilane alone possess the proper number of frequencies, namely, six for this type of molecule. Of these six frequencies, three should be polarized and three depolarized, and all the depolarized frequencies are doubly degenerate. The two triply degenerate frequencies in the regular tetrahedron type of molecule, such as silicon tetrachloride, are converted into two lines, one of which is doubly degenerate and one a single line, when the symmetry changes as from type T_d to type C_{3v} . Deuterium substitution in silicochloroform alters but very little any of the lines except for the particular vibration which may be defined as the Si—D type of linkage. This shift is decreased in silicobromoform-d as compared with silicochloroform-d.

Quartz and Amorphous Silica

If silicon oxide or silica existed according to the formula AX_2 in a linear molecule it would have the symmetry of $D_{\infty h}$ and give rise to one Raman frequency. On the other hand, if it existed as a bent molecule, it would have the symmetry C_{2v} and give rise to three Raman lines. As is to be expected this is not the case, and it is presumed that quartz and amorphous silica are actually made up of SiO_4 molecules having the tetrahedral symmetry T_d .

This compound, SiO_2 , was investigated early by Landsberg and Mandelstam,^{940, 941, 943} Hollaender and Williams,^{748, 751} Gross and Romanova,⁶⁶³ Ney,¹¹⁶⁸ I. R. Rao,¹³⁰⁵ Brickwedde and Peters,²⁷⁸ Cabannes and Bouhet,³²¹ and others. The compound index should be consulted for reference to the original work on this substance.

There should be the usual four fundamental frequencies for a compound having a tetrahedral symmetry. From the point of view of infrared absorption, Pyler has designated these as $\Delta\bar{\nu}$ 385, 488, 800 and a doublet frequency near $\Delta\bar{\nu}$ 1111 and 1190. Schaefer and Matossi and Wirtz, also from infrared absorption, consider the four frequencies as being $\Delta\bar{\nu}$ 500, 600, 800 and 900–1200, of which $\Delta\bar{\nu}$ 600 and the last-named frequency are considered three-fold degenerate. Weiler¹⁶⁶⁷ assigned to the fundamental frequencies of the SiO_4 -group $\Delta\bar{\nu}$ 502, 800, 1062–1086, and 1170–1228. He states that the entire infrared spectrum below $10\ \mu$ can be interpreted as a system

of combination bands of the second to the fourth order. He made a study of the polymeric homologs of silica esters^{1667, 1669} which shows that some of the SiO_4 frequencies are unaltered and that others are sensitive to increased polymerization. These are shown in Table 82, which will be referred to later. The observed Raman shifts in quartz and amorphous silica are included in Table 81 giving the Raman spectra of some glasses in which the composite observations on silica of different observers are included because the results are not always too concordant. In general, it may be thought that at least two of the fundamental frequencies are described by $\Delta\bar{\nu}$ 460–500 and 800. The other two are probably near $\Delta\bar{\nu}$ 630 and 1060–1170 taken as the average. It is surprising, however, in view of the large number of frequency shifts observed in quartz by Rasetti¹³³⁹ that the shift $\Delta\bar{\nu}$ 630 was not noted by him.

Cabannes and Bouhet³²¹ classify the most intense lines in quartz as three totally symmetrical, $\Delta\bar{\nu}$ 207, 356, 466, two degenerate of the first kind, $\Delta\bar{\nu}$ 266, 798 and four degenerate of the second kind, $\Delta\bar{\nu}$ 128, 394, 696, 1193.

The large number of Raman shifts is due to two reasons: first, the considerable number of lattice vibrations observed by Rasetti and, secondly, the combination frequencies and overtones which may arise from these and other Raman lines. This is somewhat of a disadvantage in determining which Raman lines are fundamentals since, with so large a number of lattice vibrations, almost any frequency can be explained on the basis of being a combination or an overtone. The situation, however, is ameliorated by the spectrum obtained from the various glasses wherein the SiO_4 -grouping tends to persist, and also by taking into consideration the intensity factors. It is to be noted that in quartz and pure silica there are lines which appear in a region lower than the fundamental, representing the lowest vibration. Polarization measurements would undoubtedly be of inestimable value in interpreting this structure.

Silicate Glasses

By a silicate glass is meant any glass which consists of silica in any combination. In addition there is included in this discussion a very limited number of glasses which contain no silica. One of these is a boric oxide glass which contains at least three important frequencies. For a complete discussion of the spectrum obtainable from boric oxide, B_2O_3 , reference should be made to Chapter 27.

A summary of all the results available on the Raman spectra of glasses is found in Table 81. For the sake of clarity it should be explained that while many of these shifts are referred to as lines, in most cases they are actually bands. The maximum intensities of the bands are referred to as the displacement values of these lines. Where the information is available

Table 81.—The Raman Shifts from Some Glasses

Composition	n _D	1	2	3	4	5	6	Raman Shifts								
								7	8	9	10	11	12	13	14	15
1 SiO ₂ (cryst.)										462(8)					693(0)	
2 SiO ₂ (cryst.)		(85)	125(10)	207(5)	265(2)	320(0)	358(2)	(394)	405(3)	463(10)	503(1)	526(0)	585(0)	633(0)	694(1)	(746)
3 SiO ₂ (amorphous)										440(10)	500(1)			625(2)	670(1)	740(0)
4 SiO ₂ (amorphous)				230	263(2)	323(4)	370(4)			450(1)	494(1)			603(1)		(720)
5 BaO ₂															700	
6 Glass (Borosilicate) 1.5165 (Crown)				208(1)	270(1)	333(1)	384(1)			454(1)	512(1)			625(2)	666(1)	740(0)
7 V.																
8 (U.V. Crown) 1.5035										480						
9 Prism Crown 1.5163										460						
10 Fluor Crown 1.4933										460						
11 Silicate Crown 1.5191										460	520(2)					
12 Dense Borosilicate Crown						340				460						
13 Telescopic Flint 1.5286										360(3)	520(3)					650(1)
14 Baryta Light Flint 1.5694										460(1)				640(1)		
15 Ordinary Light Flint 1.5774										460(1)	500(1)					
16 Baryta Light Flint 1.6042										460(3)	500(3)					
17 Ordinary Flint 1.6202										460(2)	520(2)					
18 Flint (Boro) 1.6235				208(1)	260(1)	323(2)	370(1)			450(3)	510(3)		590(1)		670(1)	740(2)
19 Plate Glass, 75% SiO ₂				268												
20 Pyrex				259						471		537		647		
21 Si, B, alk > 10%									400							
22 Si, B, alk < 10%								396		494M*			573			
23 Si, B, alk > 10%								396								
24 Si, B, alk < 10%								396								
25 Si, B, alk > 10%								396								
26 Si, B, alk < 10%								396								
27 Si, B, alk > 10%								396								
28 Si, B, alk < 10%								396								
29 Si, B, alk > 10%								396								
30 Si, B, alk < 10%								396								
31 Si, B, alk > 10%								396								
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110 Si, B, alk < 10%								396								
111 Si, B, alk > 10%								396								
112 Si, B, alk < 10%								396								
113 Si, B, alk > 10%								396								
114 Si, B, alk < 10%								396								
115 Si, B, alk > 10%								396								
116 Si, B, alk < 10%								396								
117 Si, B, alk > 10%								396								
118 Si, B, alk < 10%								396								
119 Si, B, alk > 10%								396								
120 Si, B, alk < 10%								396								
121 Si, B, alk > 10%								396								
122 Si, B, alk < 10%								396								
123 Si, B, alk > 10%								396								
124 Si, B, alk < 10%								396								
125 Si, B, alk > 10%								396								
126 Si, B, alk < 10%								396								
127 Si, B, alk > 10%					</											

Table 81.—The Raman Shifts from Some Glasses—(Continued)

Composition	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
27 Si, Pb > 10% alk < 10%		215	265M	310				400	465M		530		620		
28 SiO ₂ , Na ₂ O, BaO, B ₂ O ₃ > 10% K ₂ O, ZnO < 10%										506(5)			623(5)		
29 SiO ₂ , BaO, B ₂ O ₃ > 10% Na ₂ O, K ₂ O, Al ₂ O ₃ < 10%									496(1)				623(1)		
30 SiO ₂ , BaO, B ₂ O ₃ > 10% Na ₂ O, K ₂ O, Al ₂ O ₃ < 10%										503(1)			628(1)		
31 SiO ₂ , BaO, B ₂ O ₃ > 10% Al ₂ O ₃ < 10%									499(0)						
32 BaO, SiO ₂ , B ₂ O ₃ > 10% Al ₂ O ₃ , Na ₂ O, Sb ₂ O ₃ < 10%									498(0)				648(0)		
33 SiO ₂ , B ₂ O ₃ , K ₂ O > 10% P < 10%									485(5)				626(1)		702(1)
34 SiO ₂ , B ₂ O ₃ , Al ₂ O ₃ , K ₂ O > 10% P < 10%								475(5)	495(5)						
35 SiO ₂ , B ₂ O ₃ , K ₂ O > 10% Al ₂ O ₃ < 10%									472(5)				630(1)		
36 P ₂ O ₅ , K ₂ O > 10% B ₂ O ₃ , Al ₂ O ₃ , MgO < 10%					343(0)						535(2)		659(0)		710(5)
37 Si, K > 10% B, Al, Pb, P < 10%						380			450		530		620		(707)
38 Si, Pb > 10% alk, Al, P < 10%						360			495		530		600		(700)
39 Si, Pb > 10% SiO ₂ :PbO 2.42 alk < 10%						380					530		615		
40 Si, Pb > 10% SiO ₂ :PbO 1.51 alk < 10%						360					530		615		
41 SiO ₂ , PbO, R ₂ O > 10%* ZnO > 10%									464(3)				603(1)		
42 SiO ₂ , PbO, R ₂ O > 10% SiO ₂ , PbO, R ₂ O > 10%									457(5)						
43 SiO ₂ , PbO, R ₂ O > 10%									472(5)						

*The letter R stands for alkali.

Table 81.—The Raman Shifts from Some Glasses—(Continued)

Composition	Raman Shifts														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
44 SiO_2 , PbO , $>10\%$ BaO , R_2O $<10\%$									472(5)				623(1)		
45 PbO , SiO_2 $>10\%$ R_2O $<10\%$									482(5)				613(1)		
46 PbO , SiO_2 $>10\%$ R_2O $<10\%$									488(5)				611(0)		
47 PbO , SiO_2 $>10\%$ R_2O $<10\%$										503(5)			625(1)		
48 PbO , SiO_2 $>10\%$ R_2O $<10\%$									488(5)						
49 B_2O_3 , PbO $>10\%$ Al_2O_3 $<10\%$															
50 SiO_2 , R_2O $>10\%$ Al_2O_3 , CaO $<10\%$											535(5)				
51 SiO_2 , R_2O $>10\%$ B_2O_3 , CaO $<10\%$											522(5)		628(5)		
52 SiO_2 , R_2O , B_2O_3 $>10\%$ BaO $<10\%$										512(5)			628(5)		
53 SiO_2 , B_2O_3 , R_2O $>10\%$									486(5)				624(1)	697(1)	
54 SiO_2 , B_2O_3 , R_2O $>10\%$ Al_2O_3 $<10\%$									477(5)				616(0)	695(1)	
55 Si , Pb $>10\%$, B_2O_3 , alk. $<10\%$ SiO_2 , PbO 1.26			(240)			355					530		615		
56 Si , Pb $>10\%$, alk. $<10\%$ SiO_2 , PbO 0.805			(240)			355					530		615		
57 Si , Pb $>10\%$, alk. $<10\%$ SiO_2 , PbO 0.544			(240)			355			485		530		615		
58 Si , Pb $>10\%$, alk. $<10\%$ SiO_2 , PbO 0.452			(232)	340					485		530		600	640	
59 Si , Pb $>10\%$, alk. $<10\%$ SiO_2 , PbO 0.364			(200)	340					485		530		615		
60 SiPb $>10\%$, K, B, Sb $<10\%$ SiO_2 , PbO 0.234													(615)		
61 P, K $>10\%$ B, Al, Mg $<10\%$						350					525				720
62 Si, P, Al $>10\%$ B, Ca, Ba, Fe $<10\%$									466				610		710

Table 81.—The Raman Shifts from Some Glasses—(Continued)

Composition	n_D	Raman Shifts														
		16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
1 SiO ₂ (cryst.)			799(1)				1067(0)		1157(5)							
2 SiO ₂ (cryst.)			800(3)				1063(1)	1082(1)	1163(3)		1230(2)	(1293)				
3 SiO ₂ (amorphous)			800(5)	835(5)		1030(1)		1090(1)		1190	1240(2)	(1369)				
4 SiO ₂ (amorphous)			806(6)		(915)		1056(1)			1195(1)		(1390)				
5 BaO ₃			803(6)								1261(0)					3594(1) 4983(1)
6 Glass (Borosilicate)	1.5165		800(1)	835(1)	980(1)		1043(3)	1086(3)	1136(1)	1190(1)						
7 V																
8 (U.V. Crown)	1.5035	780						1080								
9 Prism Crown	1.5163															
10 Fluor Crown	1.4933															
11 Silicate Crown	1.5191		800(1)					1070(2)					1320(0)			
12 Dense Borosilicate Crown			800					1090(3)					1320			
13 Telescopic Flint	1.5286		800					1080								
14 Baryta Light Flint	1.5694		800(0)				1065(3)									
15 Ordinary Light Flint	1.5774	780(1)				1000(3)		1080(3)	1138(2)	1190(2)						
16 Baryta Light Flint	1.6042					1000(4)		1080(4)								
17 Ordinary Flint	1.6202					1000(3)		1080(3)								
18 Flint (Boro)	1.6235		800(2)		970(3)		1050(3)		1140(2)	1190(2)						
19 Plate Glass	785							1070			1293			1585)		
20 Pyrex	780							1071(4)			1293					
21 Si, B, alk > 10% F < 10%			800(1)	860		1030	1040				1260					
22 Si, B, alk > 10% B < 10%			800(1)	892				1070M	1175M	1265?						
23 Si, B, Sb > 10% Al, alk < 10%	780(1)				940			1070M			1200		1300			
24 Si, B, Ba > 10% Al, alk < 10%			810		940		1050									
25 Si, Ba > 10% B, Al, alk, Zn < 10%			820		946(1)			1070(3)			(1220		1350		1520)?	
26 B, Pb > 10% Al < 10%			805(4)	892				1080			1220		1370M	1520		
27 Si, Pb > 10% alk < 10%	780				960(1)	1015(1)			1130							

Table 81.—The Raman Shifts from Some Glasses—(Continued)

Composition	Raman Shifts														
	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
28 SiO ₂ Na ₂ O, BaO, B ₂ O ₃ > 10% K ₂ O, ZnO < 10%	786(0)					1067(5)									[3412(1) 4307(1) 4892(5)]
29 SiO ₂ , BaO, B ₂ O ₃ > 10% Na ₂ O, K ₂ O, Al ₂ O ₃ < 10%						1043(5)									[3359(1) 4300(1) 4899(5)]
30 SiO ₂ , BaO, B ₂ O ₃ > 10% Na ₂ O, K ₂ O, Al ₂ O ₃ < 10%					1024(5)										4300(1) 4899(5)]
31 SiO ₂ , BaO, B ₂ O ₃ > 10% Al ₂ O ₃ < 10%		825(0)			1034(5)										4370(1) 4899(5)
32 BaO, SiO ₂ , B ₂ O ₃ > 10% Al ₂ O ₃ , Na ₂ O, Sb ₂ O ₃ < 10%		825(0)				1043(5)							1443(6)		[2850(5) 3840(5) 4873(1) [3343(0) 4234(5) 4925(6)]
33 SiO ₂ , B ₂ O ₃ , K ₂ O > 10% P < 10%		802(1)		919(1)	1017(0)			1162(0)							[3840(5) 4873(1) [3343(0) 4234(5) 4925(6)]
34 SiO ₂ , B ₂ O ₃ , Al ₂ O ₃ , K ₂ O > 10% F < 10%		820(5)	898(1)		1034(1)			1127(1)					1455(1)	2850(5)	[3840(5) 4730(5)]
35 SiO ₂ , B ₂ O ₃ , K ₂ O > 10% Al ₂ O ₃ < 10%		798(1)	913(1)		1026(1)			1154(1)							[3420(1) 4245(5) 4925(6)]
36 P ₂ O ₅ , K ₂ O > 10% B ₂ O ₃ , Al ₂ O ₃ , MgO < 10%				940(1)					1183(6)			1300(5)			[3620(0) 4480(0) 5020(0)]
37 Si, K > 10% B, Al, Pb, F < 10%			(900)		1003		1070		1185			(1350– 1580)			
38 Si, Pb > 10% alk, Al, F < 10%			910		985	1055		1125				(1300– 1400)			
39 Si, Pb > 10%, SiO ₂ :PbO 2.42 alk < 10%	780			925	993	1065			1175			(1300– 1400)			
40 Si, Pb > 10%, SiO ₂ :PbO 1.51 alk < 10%	780			920	985	1055		1165				(1300– 1550)			
41 SiO ₂ , PbO, R ₂ O > 10% ZnO > 10%	789(1)			978(3)			1077(3)								
42 SiO ₂ , PbO, R ₂ O > 10%		791(1)			993(4)	1069(4)									
43 SiO ₂ , PbO, R ₂ O > 10%		796(1)			993(6)		1072(6)	1140(0)							
44 SiO ₂ , PbO, > 10% B ₂ O ₃ , R ₂ O < 10%	786(1)				981(6)	1053(5)		1130(0)							

Table 81.—The Raman Shifts from Some Glasses—(Continued)

Composition	Raman Shifts														
	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
45 PbO, SiO ₂ > 10% R ₂ O < 10%	781(0)			972(6)		1043(5)		1141(0)							
46 PbO, SiO ₂ > 10% R ₂ O < 10%	782(0)			956(6)	1020(6)			1109(0)							
47 PbO, SiO ₂ > 10% R ₂ O < 10%			889(0)	955(6)	1000(6)			1108(1)			1398(1)				
48 PbO, SiO ₂ > 10% R ₂ O < 10%			889(0)	941											
49 BaO, PbO > 10% Al ₂ O ₃ < 10%	772(1)	802(3)	905(0)			1079(0)					1360(5)				
50 SiO ₂ , R ₂ O > 10% Al ₂ O ₃ , CaO < 10%	786(1)							1102(6)							[3450(1) 4304(5) 4944(6)]
51 SiO ₂ , R ₂ O > 10% BaO, CaO < 10%		793(1)	842(0)			1097(5)									[3450(1) 4321(5) 4918(6)]
52 SiO ₂ , R ₂ O, BaO > 10% BaO < 10%		822(1)	906(1)			1074(5)	1135(0)								[3450(1) 4321(5) 4918(6)]
53 SiO ₂ , BaO, R ₂ O > 10%		800(1)		925(1)		1050(1)		1163(2)				1445(1)			[3450(0) 4321(5) 4918(6)]
54 SiO ₂ , BaO, R ₂ O > 10% Al ₂ O ₃ < 10%		809(1)		932(0)		1047(0)		1163(0)					1445(1)		[3420(1) 4245(5) 4925(6)]
55 Si, Pb > 10%, BaO, alk. < 10% SiO ₂ :PbO 1.26		820		985	1050				1175			(1370)			
56 Si, Pb > 10%, alk < 10% SiO ₂ :PbO 0.805	(780 820)		912	975	1040			1147		(1260)		1570			
57 Si, Pb > 10%, alk < 10% SiO ₂ :PbO 0.544	(780 820)		905	962	1030			1137			(1350)				
58 Si, Pb > 10%, alk < 10% SiO ₂ :PbO 0.452	780	(820)	(890)	956	1012			1127		(1220)	1370	1570			
59 Si, Pb > 10%, alk < 10% SiO ₂ :PbO 0.364	780		(885)	948	1000			1110		(1220)	1370	1570			
60 Si, Pb > 10%, K, Ba, Sb < 10% SiO ₂ , PbO 0.234	(780)		(870)		1020					(1200)		1400			
61 P, K > 10% B, Al, Mg < 10%		(800)		945					1190		1290		1450	1620	
62 Si, P, Al > 10% B, Ca, Ba, Fe < 10%	800			940	1020			1165				1320			

the index of refraction of glasses is included as well as the composition. Unfortunately, however, in many cases the composition is given only roughly by indicating the ratio of silica to one of the other principal constituents or by indicating the constituents in the glass in excess of ten per cent.

Regardless of the imposing array of results indicated in Table 81, amorphous materials have been less investigated from the point of view of Raman spectra than any other class of substance. The reason for this lies in the difficulty of eliciting Raman lines from such materials. The Raman shifts from these compounds are extremely feeble and are reminiscent of the same type of feebleness as is exhibited by compounds which are neither homopolar nor heteropolar but lie half-way between these categories. To record these results requires both optical and spectrographic arrangements which are highly efficient. Even with a spectrograph with an aperture of F:2 it requires nearly one day to record the stronger lines. Recourse cannot be had, except in the case of silica or quartz, to excitation by means of a source in the ultraviolet because these glasses will not transmit in the ultra violet region of the spectra.

The difficulty of eliciting Raman lines from glasses is not always characteristic of the glass. Hibben⁷²⁸ observed that potassium-alum glass, which exhibited no x-ray pattern corresponding to the crystals, yielded normal Raman shifts. A more complete and comprehensive examination by Hibben⁷³⁵ of organic glasses of the type exemplified by methyl methacrylate showed that this material yields Raman lines with the same facility as do the organic constituents which make up this product.

It has been shown that Raman shifts from crystals, liquids, gases and solutions are characteristic of the molecular configuration, the valence forces and the atomic masses. Since amorphous substances also possess these properties there is no *a priori* reason why they should be exceptions. In general the lines obtained from amorphous substances are broad, diffuse and can be quantitatively investigated only by microphotometric means. Furthermore, any comparison between the Raman spectra of glasses from an intensity point of view is especially difficult in view of the well-known differences in absorption which small traces of impurities will impart to these substances. This is particularly true of the lead or barium glasses and the glasses containing iron as impurity. To be recorded, the scattered radiation must necessarily pass through part of the glass itself and preferential absorption in any region will cause an alteration in the true intensity of a recorded Raman line.

It has already been indicated that one of the factors on which interpretation of these investigations is predicted is composition. In most

cases this composition is relatively unknown; in other cases the interpretation has been based on the relationship between the Raman spectra results and the infrared absorption. It has been shown in the case of the boric-oxide glasses that there is no good agreement between the two methods of approach. Until a rational coordination is obtained between the two methods, which theoretically and actually should yield completely explicable results, any explanation based on one or the other methods of procedure is open to some question. This does not mean that fundamentally there is any divergence between these two methods, but that there is something wrong either about the experimental observation or the interpretation of the results.

In the case of the glasses it remains to be demonstrated that all the experimental results are accurate, and this applies not only to the Raman spectra results but also to the infrared absorption measurements. Although these remarks are more or less confined to the negative side of this question, it still is of very material use to report the actual observations of the investigators in the case of the glasses, and to make a sincere attempt to correlate them both with the theoretical conclusions and with each other where there is a question of a difference of opinion. This leads undoubtedly to a fruitful interpretation within the limits circumscribed by the experimental conditions.

It may be emphasized, however, that notwithstanding all the deterrents, the Raman spectra method is an almost unique method of investigation for those substances which give no sharp x-ray pattern and do not yield to the usual physical-chemical methods of determining molecular constitution.

Before proceeding with a somewhat detailed discussion of the observations made on particular glasses, reference should be made to the earlier concepts regarding silica and silica glasses. From the point of view of x-ray diffraction patterns, Bragg believed that in silica the SiO_4 tetrahedra play the dominating role and that these tetrahedra are bound in various patterns. In beryl there are thought to be complex groups such as Si_2O ; in diopside, chains of SiO_3 ; in asbestos, leaves or sheaves which have the composition Si_2O_5 ; and finally in pure silica, a network structure. This network is in three dimensions and is tied together by means of the oxygen atoms closely packed in groups of four, forming the tetrahedral structure to which reference has been made, which also contains the metallic ions.

Kujumzelis⁹³¹ similarly supposes that a system of oxygen atoms is the main basis of the network structure in glasses and that within this network there is still room for other elements. The silicon atom can be replaced in a silica crystal by an aluminum atom, the only change that follows being a change in the negative charge, because the aluminum atom has a smaller

valence. The boric oxide lattice is supposed to behave like silica in forming a network, but boron cannot isomorphously replace a silicon atom in silica. The phosphorus atom also cannot replace silicon and there exist in phosphate glasses groups of PO_4 , but not arranged in continuing structure as in the silicates.

Glass itself has been looked upon as a semi-solid solution, as a mass of crystallites, as an undercooled solid solution, as a liquid, and as a colloid. It has been presumed also by Zachariasen that the forces between the atoms in a glass are the same as in the crystals. And as far as x-ray data are concerned, it has been found that in silica glass there is about the same arrangement as in cristobalite. Zachariasen further maintains that glasses consist of a network that is neither periodic nor symmetrical, in which each atom is structurally of unequal value, and that the atomic arrangement is statistically the same in every direction so that isotropy is maintained. Warren, also from x-ray measurements, comes to the conclusion that the maximum of these scattering curves from glasses having a low sodium content agrees with that of silica. With increasing introduction of sodium into the glass this maximum is wiped out and another takes its place, becoming increasingly stronger as the sodium concentration increases. These results are in favor of the hypothesis of Zachariasen in regard to the existence of a network throughout the glass and in opposition to the crystallite theory. This new maximum would, therefore, belong to the coordination of the oxygen atoms oriented around the sodium atom.

Kujumzelis⁹³¹ believes that the Raman spectra of the network structure in a glass must result in a continuous band on which are superimposed the Raman frequencies of the various chemical combinations present. It is his belief that a band, which will be referred to later, extending from near the exciting line to approximately $\Delta\bar{\nu}$ 550, corresponds to the vibration of this network. It is believed further that the sharp boundary of this band indicates that there is a limiting frequency for the external vibrations of this network structure. Values of the limiting frequencies depend on the composition of the glass.

It is, of course, quite evident that all the frequencies observed in the glasses cannot be assigned to the SiO_4 -group. There exists then the possibility of superimposition of other frequencies of other definite complex groups on the SiO_4 -group. The internal Raman spectra then depend on all the atoms that go to make up the glasses, particularly the oxygen and other elements which, from their size or their mass, tend to have a pronounced effect on the total spectra of the glasses.

Of course, the change in spectrum of the glasses could be looked upon as simply a change in the vibration of the SiO_4 tetrahedron brought about by the influence of the other atoms. Neither Kujumzelis⁹³¹ nor Langen-

berg⁹⁴⁷ believes that this interpretation is in conformity with the observations, because the intensity of the shift of these frequencies, as observed in quartz, silica glass, and glasses in which the SiO_2 contents dominate, is quite different and bears little relation to the SiO_2 concentration.

Consider first the series of glasses, numbers 6 to 16 in Table 81, which were studied by Bhagavantam.¹³⁶ It is apparent immediately that most of the lines observed are similar to those observed in either amorphous silica or crystalline quartz. Absence of particular frequencies cannot be given great weight. It may be stated, however, that those glasses which have a high index of refraction show relatively greater intensity in the band near $\Delta\bar{\nu}$ 1000 and $\Delta\bar{\nu}$ 1080 than the earlier members of the series. The same may be said of a band lying between $\Delta\bar{\nu}$ 460 and 500. However, the relative intensity between these two groups ($\Delta\bar{\nu}$ 460–520 and 1000–1080 as observed in quartz) suffers a reversal in passing from the lower index glasses to the higher, although the absolute intensity of both groups is less in the former. Although it is pure speculation, the increasing intensity of the Raman shifts with increasing index of refraction may possibly be attributable to the closer approach of the exciting radiation to the characteristic ultraviolet absorption of these glasses. This is in line with the type of optical catalyzers discussed under the section devoted to technique. In some of the glasses investigated, frequency shifts have been reported in the neighborhood of $\Delta\bar{\nu}$ 1600. Hollaender and Williams⁷⁴⁸ also report a shift near $\Delta\bar{\nu}$ 2309. It is probable that both of these shifts are erroneous. Nevertheless, if they really exist they could be attributed to combinations or harmonics, particularly the $\Delta\bar{\nu}$ 1600 which could occur as a harmonic of $\Delta\bar{\nu}$ 800. In view of the low intensity of these Raman lines, it would not seem probable that a harmonic should exist in this region of the spectrum.

Consider next the work of Langenberg.⁹⁴⁷ This author has investigated glasses 28 to 36 and 41 to 54 inclusive, reported in Table 81. Let us first discuss the group of glasses designated by numbers 41 to 48 inclusive. These results tend to show a decrease in the SiO_4 frequency ascribed to $\Delta\bar{\nu}$ 806, to a minimum value of $\Delta\bar{\nu}$ 782 in the lead-silica glasses. A similar decrease is noted also in $\Delta\bar{\nu}$ 1056 and 1195 which are both reduced to $\Delta\bar{\nu}$ 1000(8) and to 1108(0). At the same time there is presumably an appearance of a new frequency which starts in at $\Delta\bar{\nu}$ 978 and finally reduces to 955. With the exception of $\Delta\bar{\nu}$ 955 other frequencies can be ascribed to the SiO_4 -group as modified by the change in environment.

Another group of glasses investigated are those listed under numbers 49 to 54 and 33 to 36 inclusive, whose composition is made up chiefly of silica, boric oxide and an alkali or an alkaline earth. One of these, an alkali glass (50), contains no boric oxide. The spectrum from this glass is essentially the same as that observed from silica with the exception of

$\Delta\bar{\nu}$ 603 and 1195, which are missing. This absence, however, is probably without significance, as these are among the weakest lines observed from the pure silica.

As has been mentioned, Glass 5, or boric oxide glass, contains three significant Raman lines. The effect of combining boric oxide with silica is to alter slightly the principal lines of both of these compounds. The strongest line, $\Delta\bar{\nu}$ 806, unfortunately overlaps one of the strongest lines of silica at $\Delta\bar{\nu}$ 803. In glasses 52 and 53, there is an appearance of a line of fair intensity near $\Delta\bar{\nu}$ 1445 which is assigned to the boric oxide component of the glass. As there is a weak frequency in this region in both boric acid and sodium tetraborate, this probably may be assigned correctly to a vibration of the BO_2 -groups. The line which appears at $\Delta\bar{\nu}$ 464 in pure silica (Langenberg reports this as 494) changes to $\Delta\bar{\nu}$ 535 in the pure alkali silicate glass and gradually reverts to $\Delta\bar{\nu}$ 477 in the borosilicate glasses. There is also a decrease in intensity of $\Delta\bar{\nu}$ 638, which appears in Glasses 50 to 54, as well as in many others. The shift at $\Delta\bar{\nu}$ 915 is considered by Langenberg to be a displacement of the $\Delta\bar{\nu}$ 803 in pure boric oxide. This would seem a reasonable assumption, as this appears at $\Delta\bar{\nu}$ 905 in Glass 49 which is primarily a lead-boric oxide glass containing no silica. The frequency at $\Delta\bar{\nu}$ 1360 is attributed also to an altered shift from $\Delta\bar{\nu}$ 1261 in Glass 49. Introduction of an alkaline earth such as barium oxide causes the change of $\Delta\bar{\nu}$ 512 to 486 as is noted in Glasses 53 and 54, and the introduction of barium also causes alteration of the frequency near $\Delta\bar{\nu}$ 1070 to 1050. The addition of alumina into the borosilicate glass causes a decrease from $\Delta\bar{\nu}$ 919 in Glass 33 to 889 in Glass 34.

Glasses having a high lead content such as Glasses 41 to 48 have a somewhat altered spectrum. In the only phosphate glass investigated by Langenberg there occur the $\Delta\bar{\nu}$ 343, 534, 659, 940 and 1300 shown in Table 81 as Glass 36. With the exception of $\Delta\bar{\nu}$ 659, these frequencies agree reasonably with those observed in phosphoric acid and the phosphates. The line at $\Delta\bar{\nu}$ 1300 is attributed to the P—O vibration. The two lines, $\Delta\bar{\nu}$ 710 and 1183, both of which appear as strong lines, can be assigned to phosphoric acid or to a vibration of the BO_2 -group.

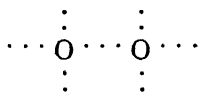
The frequencies which appear between $\Delta\bar{\nu}$ 3000 and 5000 are considered by Langenberg to be Raman lines, but by Kujumzelis^{930, 931} to be fluorescent bands. It would appear that the latter interpretation is probably correct.

Kujumzelis has investigated a number of glasses of varying composition. These are shown in Table 81 as Glasses 21 to 27, 55 to 62, and 37 to 40 inclusive. These observations differ from others principally in the appearance of broad bands in the region between $\Delta\bar{\nu}$ 200 and 300, and in considering the shift between $\Delta\bar{\nu}$ 450 and 550 as consisting of a single band with a

maximum usually occurring near $\Delta\bar{\nu}$ 500. Of the bands observed there are only two which might be considered reasonably sharp. These are lines at $\Delta\bar{\nu}$ 650 and 800. The glasses which show Raman shifts less than $\Delta\bar{\nu}$ 300 all contain lead, with the exception of Glass 60, although this glass has a higher lead content than any of the others. Furthermore, the glasses which show a Raman shift near $\Delta\bar{\nu}$ 380 usually contain lead. However, Glasses 21, 22, 23 and 61 do not contain lead although a shift is present near $\Delta\bar{\nu}$ 380. Glasses 21 and 22, containing alkali, boron and silicon as oxides in concentrations greater than 10 per cent, exhibit a broad band extending from $\Delta\bar{\nu}$ 396 to approximately $\Delta\bar{\nu}$ 573 in Glass 21 and to $\Delta\bar{\nu}$ 550 in Glass 22. The intensity maximum also varies between these two glasses. In Glass 23 this broad band begins at $\Delta\bar{\nu}$ 380 and terminates at 500 with an intensity maximum at 450. Glasses 24 to 27 all show bands in the region below $\Delta\bar{\nu}$ 550. However, Glasses 24, 25 and 26 exhibit much sharper lines than the others so far mentioned. There is a progressive increase of the maxima in these three glasses, beginning at $\Delta\bar{\nu}$ 400, then changing to 485 and finally to 510.

Suppose Glasses 39 and 40 and 55 to 60 inclusive are considered next. These represent increasing quantities of lead oxide in relation to the silica content of the glass. Compare first Glass 37 with Glass 38, which differ chiefly in the replacement of potassium by lead. There follows a decrease in $\Delta\bar{\nu}$ 1003, 1070, and 1185 to $\Delta\bar{\nu}$ 985, 1055, and 1125 respectively in the lead glass. As the lead content is increased relative to the silicon content, the value of these shifts decreases in magnitude by a factor which approximates 60 wave numbers in all cases. Furthermore, $\Delta\bar{\nu}$ 985, in the lead glass designated as 38, is split in Glass 39 into two components beginning with $\Delta\bar{\nu}$ 925, and ending in 993. If less than ten per cent of boric oxide is also introduced into glass, as illustrated by Glass 55, the effect of the lead in altering the frequencies between $\Delta\bar{\nu}$ 900 and 1200 is less pronounced, presumably because there is a certain compensation in replacing the large, heavy, divalent lead ion by the light, small, trivalent boron ion.

Turning again to discuss the frequencies appearing at less than $\Delta\bar{\nu}$ 900, it is obvious that there are two frequencies near $\Delta\bar{\nu}$ 610 and 800 which appear at approximately this value in all the glasses and in both quartz and silica. There is, furthermore, a very little alteration in either the sharpness or intensity of these vibrations on replacing silica in the glass by larger amounts of lead oxide. The vibrations are assigned by Kujumzelis to vibrations involving an arrangement of the oxygen atom as illustrated below.



The doubling of this frequency in crystalline quartz or in fused silica is accounted for on the basis of a superposition of the two frequencies, one, the vibration of the oxygen atoms as just noted and, two, the vibration of the regular SiO_4 tetrahedron. The vibration of this tetrahedron throughout the entire glass cannot be compared with similar vibrations of the SO_4 - or CCl_4 -groups. Some confirmation of this hypothesis is to be found in the frequency shift at $\Delta\bar{\nu}$ 808 in boric oxide which also would present a similar type of oxygen-to-oxygen vibration. In boric oxide, therefore, a close packing of oxygen atoms is possible; but within this arrangement are contained boron atoms. The type of binding in the groups referred to, or between tetrahedra, is not considered by Kujumzelis to be a purely chemical, but a coordinated binding. In the case of phosphate glasses there is an entirely different relationship between the oxygen and the phosphorus atoms as compared with SiO_4 . The lines in the phosphate glasses are sharp and intense. In boric oxide glass the second line is near $\Delta\bar{\nu}$ 1265. It is much weaker than the one observed at $\Delta\bar{\nu}$ 806 and is attributed to a $\text{B} \leftrightarrow \text{O}$ vibration. In glasses having a high lead content the frequency possibly appearing near $\Delta\bar{\nu}$ 200 is assigned to the $\text{Pb} \leftrightarrow \text{O}$ vibration. Some confirmation of this assignment is to be found in the infrared spectra measurements on a number of borates and oxides by Parodi, who observes reflection and transmission bands in the $\Delta\bar{\nu}$ 265 to 446 region. Kujumzelis lays great emphasis on the lower frequency shifts occurring between $\Delta\bar{\nu}$ 300 and 600 which, according to him, are superposed on a background somewhat continuous in nature.

It is difficult to compare the work of Langenberg with that of Kujumzelis in this respect. Nevertheless, in general, it can be stated that Langenberg has not observed any frequency in the glasses which would fall in the region less than $\Delta\bar{\nu}$ 400. In the types of glass which have been investigated by both workers, such as Glasses 22 and 53, Kujumzelis finds that the maximum of the band appearing between 396 and 573 occurs at 520. Another example may be chosen simply to illustrate the difference in the results of these two observers. In Glass 29, considered by Langenberg to be essentially a barium borosilicate glass, there is noted in the spectral region less than $\Delta\bar{\nu}$ 600 only one line at $\Delta\bar{\nu}$ 496. Kujumzelis on the other hand has observed in Glass 24, of similar composition, two shifts, $\Delta\bar{\nu}$ 400 and 503. These results are not necessarily antagonistic, but they do serve to illustrate the fact that different observers get different results with glasses which may be considered as having approximately the same composition. The results also illustrate that composition will influence the Raman spectra obtained from the barium glasses.

A glass then, according to Kujumzelis, consists essentially of oxygen atoms which are jointly attached to one another and to the glass-forming

elements boron, silicon, etc., with a "coördination" valence rather than by purely chemical means. The inner vibrations of definite complex groups reveal themselves as Raman frequencies and are influenced by both the kind and the number of participating atoms. Each one of these groups may be oriented in a different direction and the groups, therefore, do not contribute to a sharp x-ray pattern. Since there is no periodic repetition of the proposed network, the outer vibrations correspond to a continuous spectrum which diminishes after reaching a sharp maximum frequency.

For the purpose of recapitulation at this point, it would be advisable to reexamine these results in somewhat general terms. With the exception of lattice vibration in quartz—or for that matter in amorphous silica—the most intense Raman line observed occurs near $\Delta\tilde{\nu}$ 465. In some of the glasses this appears as a doublet frequency about $\Delta\tilde{\nu}$ 460 and 520, both bands being of approximately equal intensity. In addition to these lines, Kujumzelis⁹³⁰ observes a band of considerable intensity in lead silicate glasses, which is made up of at least three components between $\Delta\tilde{\nu}$ 960 and 1175. In glasses consisting chiefly of silica borosilicate and barium borosilicate type this tends toward a single band with a maximum at 1070. In general the more prominent lines of silica persist in all the glasses together with the appearance of additional lines and modifications of intensity depending on the variations in composition.

Bhagavantam has indicated some change in the Raman spectra of glasses depending on the index of refraction. As this index varies with composition, this is another way of saying that the spectrum changes with composition. In these cases the true composition is unknown; consequently little can be said in regard to the spectrum except to point out its modifications in a very general sense.

The work of Kujumzelis and Langenberg differs in some important details. There is first the question of the frequency shifts appearing between $\Delta\tilde{\nu}$ 3000 and 5000 which are reported by Langenberg to be Raman lines and are considered by Kujumzelis to be fluorescent bands. The evidence is not entirely conclusive.

These experimental results, together with the tentative conclusion derived from them, have been presented in some detail; first, because there has been very little work done on these types of compound; secondly, because of divergencies in the experimental results; and thirdly, because these observations are capable of more than one interpretation.

The recent work of Hibben on the structure of water wherein it was shown that there is a definite force of attraction between the water molecules, and that this force may give rise to specific Raman lines, is some evidence in favor of the concept of the continuing structure or network in the silicate and borate glasses. As has been mentioned already, he has

shown also that in organic glasses many of the Raman lines for the monomer remain unaffected after polymerization to a glassy polymer. The lines which are affected are those which would take a definite part in the production of the organic glass. Even in the case of water or ice the effective pattern of the water molecules is not altered enormously, although new lines corresponding to the intermolecular attraction and hindered rotation appear. These seem to be, in general, the origin of some of the bands in the glasses. The general pattern of crystalline quartz is shown in all the glasses containing silica. In some cases then, where there is introduction of a sufficient quantity of another element such as lead oxide, this may result in the appearance of a line corresponding to this oxide, or in the alteration of the higher-frequency shifts of the silica component. Some of the lower-frequency shifts near $\Delta\bar{\nu}$ 200 or 300 may owe their origin to the intermolecular vibration or hindered rotation of the tetrahedral unit composing the glass. This is essentially the oxygen vibration which Kujumzelis has assigned to $\Delta\bar{\nu}$ 800. It is thought that the lower-frequency shift for this type of vibration would be the more plausible assignment.

Complex Compounds of Silica

Reference previously has been made to the group of ester derivatives of silica investigated by Weiler.¹⁶⁶⁹ These begin with the tetramethyl ester of SiO_4 and conclude with the decameric compound which contains ten silica atoms and 22 methyl groups. These results are shown in Table 82. These lead, according to Weiler, to the determination of the four fundamental frequencies attributable to the SiO_4 -group. Disregarding the Raman lines which owe their origin to the methyl group, there appear two lines, one $\Delta\bar{\nu}$ 1086 and one near $\Delta\bar{\nu}$ 1195, which remain constant in all these derivatives. In the monomer the spectrum is more complex and gives rise to a group of lines or bands between $\Delta\bar{\nu}$ 1080 and 1132. In the higher derivatives, however, there appear only these two bands referred to above. In addition to these one band occurs near $\Delta\bar{\nu}$ 842 in the monomer, which is reduced slightly to $\Delta\bar{\nu}$ 825 in the highest polymer. The fourth line begins with $\Delta\bar{\nu}$ 642 in the monomer but is reduced to 518 in the decamer. The stepwise reduction is quite noticeable. These results are helpful in determining at least some of the characteristic frequencies of the SiO_4 -group. As has been mentioned there is some doubt as to defining the fundamental frequencies of the SiO_4 -group. According to these results the frequencies would average approximately $\Delta\bar{\nu}$ 600, 850, 1100, and 1200. So far as the other compounds in the table are concerned, from phenacite to tourmaline, these seem to indicate a frequency in the $\Delta\bar{\nu}$ 1150 region in one or two cases, but the correlation between these observations and an SiO_4 -group as previously outlined is dependent principally on the reasonably

strong frequencies near $\Delta\tilde{\nu}$ 840 to 876. However, there are in some cases frequencies near $\Delta\tilde{\nu}$ 440 and 520, as observed in silica, as well as a number of intense shifts that correspond to lattice vibrations.

According to Kopcewicz⁸⁹³ topaz gives $\Delta\tilde{\nu}$ 174, 223, 258, 916, 1053 at 500° C. which is slightly changed from $\Delta\tilde{\nu}$ 189 and 270 as a function of temperature. In the case of beryl, the major changes are from $\Delta\tilde{\nu}$ 235, 709, 1002 at 20° C. to 221, 697, 998 at 500°.

Chakravant and Ganguli³⁵⁴ have investigated $\text{Na}_2\text{O}:\text{SiO}_2$ (ratio 1:2) and sodium silicate (ratio 1:4); they dialysed solutions of silicic acid and found that they all yield $\Delta\tilde{\nu}$ 261 which is one of the shifts observed in silica. This spectrum is undoubtedly incomplete.

Notwithstanding the careful work of Nisi,¹¹⁸¹ it can be concluded that the general result from the complex oxides of silica is indeterminate. In all of these, for example, more frequency shifts have been recorded than probably exist. Furthermore, some of the higher frequency shifts noted in excess of $\Delta\tilde{\nu}$ 3400 are open to question as to whether these are truly Raman lines or fluorescence bands. In the case of topaz some alteration in the intensity of the Raman lines is considered to be dependent on the direction of illumination and the direction of observation of the crystals. In agreement with Nisi himself, it may be stated that the experimental data which have been obtained so far in the Raman spectra studies of these crystals are too scanty to find any completely definite relationship between the crystal spectra and the frequency of the Raman lines. On the whole it may be stated that possibly in the complex silicates the principal shift of the intense lines, which seems to correspond to the inactive vibration of the SiO_4 -group, increases with the valence of the metal ions; for example, in phenacite this is $\Delta\tilde{\nu}$ 876; in topaz, 925, and in zircon, 1006.

The entire group of crystals so far investigated yield Raman spectra data which do not permit a satisfactory interpretation in terms of structure. When, however, it is considered that these have been investigated by only one or two workers, and that in most cases a complete interpretation of Raman spectra results has been the outcome of numerous investigations by different people under different conditions, it is reasonable to assume that if this field is further explored more conclusive evidence can be obtained by this method.

Chapter 27

The Raman Spectra of Diverse Oxides and Azides

The various oxides discussed in this chapter are those which have not been discussed elsewhere in detail. The sulfates, perchlorates and phosphates, for example, are discussed in Chapter 14. This is because their relationship to the acids is of greater interest than their existence as oxides. On the other hand, boric acid and its oxides are dealt with in this chapter because the salts of boric acid are of greater interest than the acid itself.

The azides are included with the nitrogen oxides in order to make a comparison of their structures.

Carbonates

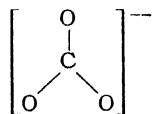
The strongest line observed in the carbonates in solution occurs at approximately $\Delta\bar{\nu}$ 1065, and is displaced to a slightly greater value in crystals. In general the carbonate ion has been considered as a plane structure of the type AB_3 having the symmetry D_{3h} or, in other words, an equilateral triangle with the carbon atom in the center. This differs from the pyramidal structure only in the sense that the height of the central atom in relation to the plane of the other atoms is zero. There is a decrease of approximately 30 wave numbers in the principal frequency in potassium acid carbonate as compared with potassium carbonate. In both lead carbonate and calcium carbonate there has been observed a considerable number of other shifts, many of which, particularly in calcite or aragonite, can be ascribed to lattice vibrations. These results are shown in Table 83. Items 6 and 7 are taken principally from the work of Rasetti (1339) and items 5 and 8 are from the observations of Hibben.⁷⁴² There is fair agreement in the value of the Raman shifts for those lines observed by both. Hibben, however, has recorded a group of four lines between $\Delta\bar{\nu}$ 2000 and 2900 previously unobserved. The three principal lines in the carbonate group are those occurring at $\Delta\bar{\nu}$ 710, 1072, and 1429. Of these, the first and last are doubly degenerate and $\Delta\bar{\nu}$ 1072 represents the symmetrical oscillation. These are fairly close to the Raman shifts observed in the nitrates, which have a similar constitution. Kujumzelis observes $\Delta\bar{\nu}$ 680 in solution, which presumably corresponds to $\Delta\bar{\nu}$ 710 mentioned above. The fourth frequency, observable in infrared absorption, should occur near $\Delta\bar{\nu}$ 860 but it is not active in the Raman effect. Most of the other Raman

lines observed are probably combination frequencies. If the ν_4 oscillation is assigned to $\Delta\bar{\nu}$ 710 then the shift at $\Delta\bar{\nu}$ 2145 could be accounted for as $3\nu_4$ and, if $\Delta\bar{\nu}$ 1072 is assigned to ν_1 , then $\Delta\bar{\nu}$ 2145 could also be a combination of $2\nu_1$. Similarly the shift at $\Delta\bar{\nu}$ 2856 would represent the fourth harmonic of ν_4 , and $\Delta\bar{\nu}$ 2300 is a combination of $3\nu_4$ and the lattice vibration at 158. It should be mentioned that the three lattice vibrations at $\Delta\bar{\nu}$ 86, 157, and 280 occur as anti-Stokes lines with almost the same intensity as the Stokes lines. This has been noted also by Kimura and Uchida,⁸⁰⁹ Venkatesachar and Sibaiya,¹⁶⁰⁶ Nisi¹¹⁷⁶ and others. Kopcewicz⁸⁹³ notes that the lines at $\Delta\bar{\nu}$ 157 and 280 in calcite are reduced by ten wave numbers if the temperature is increased by about 400° C., while 714 and 1430 decrease five wave numbers. The $\Delta\bar{\nu}$ near 1090 or 1072 and 1747 are unchanged. For the lattice vibrations the diminution is according to the following formula:

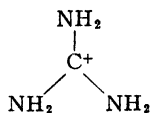
$$\Delta\bar{\nu} = \frac{A}{\nu} \cdot \frac{\partial a}{\partial T} \Delta T$$

where A 1.94×10^6 , T = temperature, $\frac{\partial a}{\partial T}$ = the atomic displacement in centimeters and ν the observed vibration in reciprocal centimeters.

Thus far in this discussion the carbonate ion has been structurally represented by the configuration

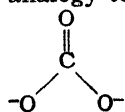


This is similar, in principle, to one of the structural representations of the guanidonium ion, namely,

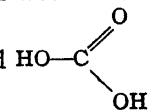


discussed previously in the organic section under the amides. Here it was

pointed out that the configuration $\text{H}_2\text{N}^+=\text{C} \begin{array}{l} \text{NH}_2 \\ \text{NH}_2 \end{array}$ in which the $\text{N}=\text{C}$ resonates among all three groups was also possible. Continuing this analogy to the carbonate group, this would indicate the possible structure



for the carbonate ion and



for carbonic acid similar

to $\text{HO}-\overset{+}{\text{N}} \begin{array}{c} \nearrow \text{O} \\ \searrow \text{O} \end{array}$ for nitric acid. Carbonic acid has not been investigated so

it is not possible to draw any conclusion regarding the presence of a carboxyl group. The shift at $\Delta\tilde{\nu}$ 1740 which has been ascribed to the $\text{C}=\text{O}$ linkage appears weakly in the carbonate ion. This has also been attributed, however, to the first harmonic of the fundamental $\Delta\tilde{\nu}$ 860 which is forbidden in the Raman effect.

Boron Oxides

Boric oxides, like silica, may exist in both the crystalline and amorphous states. The boric oxides, also like silica, may combine with the alkalis to produce a variety of crystalline or amorphous compounds and solutions. Although silica has been investigated with both spectrographic and diffraction pattern methods, it is only recently that boric oxide, boric acid and boric acid salts have been examined by Raman spectra methods.

Silica, as is well known, does not correspond to the triatomic form molecule having the formula SiO_2 but rather exists in the crystalline and amorphous states as a tetrahedral molecule having the symmetry T_d and the effective constitution corresponding to SiO_4 .

With the boric oxide compounds the situation is quite different. Here it is possible to have a molecule of the type ABA representing the metaborate ion, which in the linear form would have the symmetry $C_{\infty v}$ and give rise to but a single Raman line. On the other hand, the molecule may be bent, in which case the symmetry would be C_{2v} and there should appear three Raman frequencies corresponding to the ν_r , ν_s , and δ_r types of oscillation. For boric acid the most probable arrangement would be a molecule of the type AB_3 having the symmetry D_{3h} in which all three B groups would lie at the corners of a plane triangle with the A atom in the center. This is similar to the arrangement of the NO_3 -group in the nitrate ion and the CO_3 -group in the carbonate ion. This configuration would give rise to three Raman lines, two of which would be doubly degenerate, and one symmetrical frequency which would correspond to the symmetrical expansion and contraction of the molecule.

Recently Ananthakrishnan³⁸ observed for boric acid in solution only one line at $\Delta\tilde{\nu}$ 855(3), and for the crystalline boric acid two additional frequencies near $\Delta\tilde{\nu}$ 3180(3) and 3256(1). These are similar to the observations of Kahovec⁷⁸⁶ and Mitra. In the crystalline boric acid, Nielsen¹¹⁷³ has observed other frequencies, $\Delta\tilde{\nu}$ 503(4), 1065(0), and 1155(0). Of these frequencies, those in the $\Delta\tilde{\nu}$ 3000–3600 region are connected solely with the $\text{O} \leftrightarrow \text{H}$ oscillation. These results, together with the new observa-

tions of Hibben⁷³⁶ and other Raman spectra data on boric acid and its derivatives, are shown in Table 84.

Ananthakrishnan attempts to correlate the largest pair of frequencies observed by him with a "hydroxyl bond" in contradistinction to a "hydrogen bond." The evidence for this distinction is not well founded, first, because the O—H frequency is present, presumably in acids supposed to exhibit hydrogen bonding, and second, because the diminishing of the O—H frequency in the alkali hydroxides from $\Delta\bar{\nu}$ 3600 to 3300, or less, does not seem to be significant of any hydroxyl bonding. The same reduction in the typical O—H shift occurs in most crystal hydrates.

In addition to the intense line at $\Delta\bar{\nu}$ 875 in an aqueous solution of boric acid, Hibben⁷⁴⁰ has observed also two other lines of fair intensity at $\Delta\bar{\nu}$ 506(2) and 1420(1). These two frequencies are broad and diffuse. There occur, furthermore, two lines—or possibly one band—at $\Delta\bar{\nu}$ 1060 and 1130. If this were a single band the intensity center would be near $\Delta\bar{\nu}$ 1100. These two bands (or band) are exceedingly weak, and probably correspond to the equivalent frequencies seen in the crystals, where they appear as reasonably sharp lines, although with intensities that are very feeble. Mitra¹¹¹⁵ on the other hand does not observe $\Delta\bar{\nu}$ 1420 in a saturated solution of boric acid, but does record $\Delta\bar{\nu}$ 515, 872, and 986, in dilute solutions $\Delta\bar{\nu}$ 710, 872, 909 and 1340. These are not included in the table because these results should be confirmed.

It is to be noted that on the whole the spectrum obtained from boric acid solutions is approximately identical with that observed in the crystals, with the exception of the line attributable to the O—H oscillations which are naturally masked in aqueous solutions by the O—H vibrations of the water molecule. From this similarity one may reasonably draw the conclusion that boric acid in solution contains the O—H group attached to the boron atom and that there is no possibility of the existence of a molecule having the form H_3BO_3 . This is substantiated further by the lack of any B—H line corresponding to the P—H line found in H_3PO_3 . There exist, then, three frequencies for boric acid which are beyond dispute, namely, $\Delta\bar{\nu}$ 506, 873, and 1420. This last frequency shift differs too widely from a combination of $\Delta\bar{\nu}$ 873 with 506 to be a combination frequency. The relative grouping and intensity of these three lines are reminiscent of the three Raman shifts at $\Delta\bar{\nu}$ 710, 1050, and 1340 observed in the nitrate ion.

Consider next the simplest salt of boric acid, sodium metaborate. In solution this was originally supposed by Ghosh and Das⁵⁹⁸ to yield $\Delta\bar{\nu}$ 253(1) and 1403(4), while Nielsen and Ward¹¹⁷⁴ reported $\Delta\bar{\nu}$ 749. More recently, Nielsen¹¹⁷³ has observed an additional line at $\Delta\bar{\nu}$ 950(1). Hibben⁷³⁶ also finds $\Delta\bar{\nu}$ 747(6) and in addition, the broad band extending from $\Delta\bar{\nu}$ 1132 to 1276 which may be made up of two separate diffused lines. The band

reported from $\Delta\bar{\nu}$ 400 to 500 in Table 84 is undoubtedly the hindered rotational band observed in water. Crystalline sodium metaborate tetrahydrate, according to Nielsen ¹¹⁷³ yields $\Delta\bar{\nu}$ 741(5) and two frequencies at $\Delta\bar{\nu}$ 3190(1) and 3555(1). These last two frequencies are connected with the hydroxyl group in the hydrated crystals, while no other frequencies were observed between $\Delta\bar{\nu}$ 741 and 3190. They are probably in existence but are too difficult to discern when small crystals are used.

The principal and probably the symmetrical vibration, therefore, of the metaborate ions occurs at $\Delta\bar{\nu}$ 747. This is present not only in solution but also in the crystals, although in the latter it is reduced by a few wave numbers. This same frequency also occurs in sodium tetraborate whose spectrum will be discussed shortly. It is obvious that the spectrum of sodium metaborate differs widely from that observed in boric acid. It was supposed originally that the BO_2 ion represented a linear grouping of a molecule of the type ABA. The appearance of additional Raman lines, however, would make this an impossibility for the reasons already mentioned in discussing molecules having the symmetry C_{2v} and a bent structure. An example of this type of molecule is sulfur dioxide which shows three principal Raman lines at $\Delta\bar{\nu}$ 525, 1144, and 1334, of which the middle frequency is the most intense. Zachariasen, from x-ray measurements, has concluded that the anhydrous metaborate exists in a ring formation somewhat similar to the benzene ring with alternating boron and oxygen atoms. If this structure persisted in solution it would exist as a B_3O_6 ion. The principal objection to such a hypothesis is a dearth of Raman lines. Such a structure could possibly have 21 different frequency shifts. The symmetry conditions would undoubtedly reduce this number by a considerable amount, but it seems likely that the number would exceed one or two Raman lines.

In the spectra observed from sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, obtained as kernite or borax, Nielsen ¹¹⁷³ has found about four lines in borax of equal intensity, in addition to the group of three attributable to the water molecule in the crystal hydrate. Hibben ⁷⁸⁶ likewise has observed a group of similar lines in kernite with the exception of $\Delta\bar{\nu}$ 891 and inclusive of a strong line at $\Delta\bar{\nu}$ 735 which was not noted by Nielsen. This shift is slightly reduced from the value near $\Delta\bar{\nu}$ 747 in the solution of sodium tetraborate. Curiously enough, this shift was reported by Jogelkar and Thatte ⁷⁸¹ for ammonium tetraborate in the crystalline form at $\Delta\bar{\nu}$ 714. At the same time, however, no shift was noted by them at $\Delta\bar{\nu}$ 934. From the intensity observed for this line, it apparently is the type of vibration equivalent to that which occurs near $\Delta\bar{\nu}$ 875 but is displaced to a higher frequency in the crystals. The spectrum obtained from the saturated solution agrees fairly well with that observed in the crystals with the exception

of the possible splitting of $\Delta\bar{\nu}$ 875 into several components. There is also a weak band which may be made up of a pair of lines near $\Delta\bar{\nu}$ 1000 and 1130. The actual magnitude of these shifts can be only estimated, as these bands are too feeble and too diffuse to measure with accuracy.

The question may be raised as to why such a strong pair of lines at $\Delta\bar{\nu}$ 747 and 875 should appear from an aqueous solution of sodium tetraborate when the metaborate possesses only one strong line, and boric acid similarly has only one. Furthermore, the second strong line in the tetraborate coincides with that observed from boric acid. In fact, the entire spectrum of sodium tetraborate resembles, or is identical with, the combined spectrum of boric acid and sodium metaborate. Another peculiarity is the extreme intensity of the line at $\Delta\bar{\nu}$ 3552 in the tetrahydrate. This line is much stronger than the usual lines that may be attributed to water of crystallization, and appears near the observed shift for the OH-group in boric acid. This would seem to indicate the possibility of an actual hydroxyl group of constitution being present in the crystalline tetraborate. This is shown in the microphotometer tracing in Figure 69.

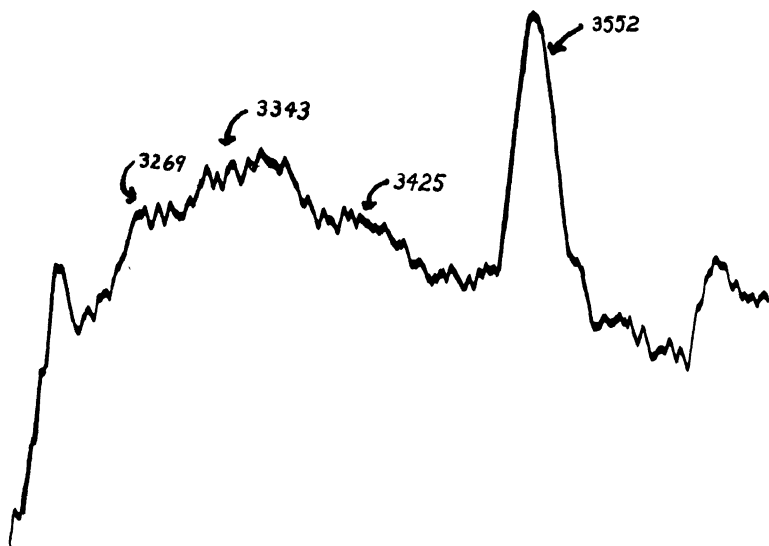


FIGURE 69. The O—H Shifts in Sodium Tetraborate Tetrahydrate.

In an attempt to throw some light on this subject, Hibben⁷⁴⁰ initiated a series of studies of solutions of boric acid containing variable amounts of sodium hydroxide. The results of these experiments are indicated in Figures 70 and 71, which show not only the effect of the addition of sodium hydroxide to boric acid, but also give a comparison spectrum of the crystal-

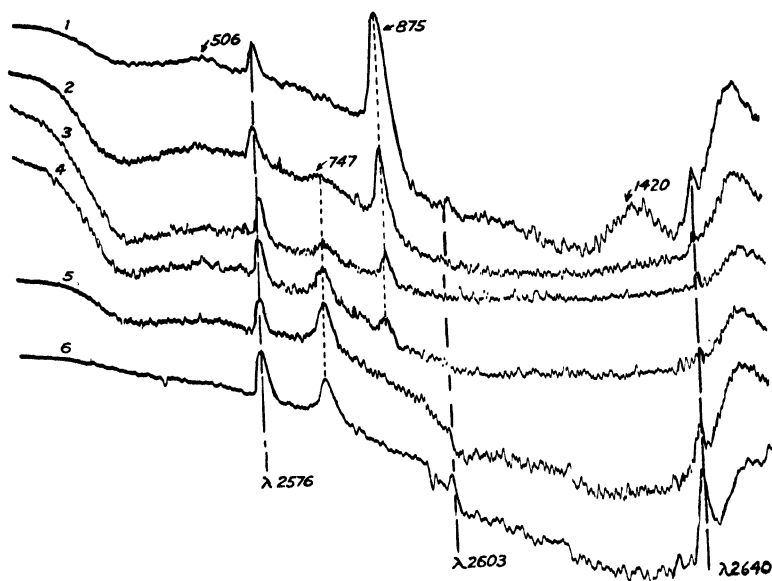


FIGURE 70. Conversion of Boric Acid to Sodium Metaborate as Shown by Raman Spectra. Lines 2 to 6 represent the addition of sodium hydroxide in increasing amounts.

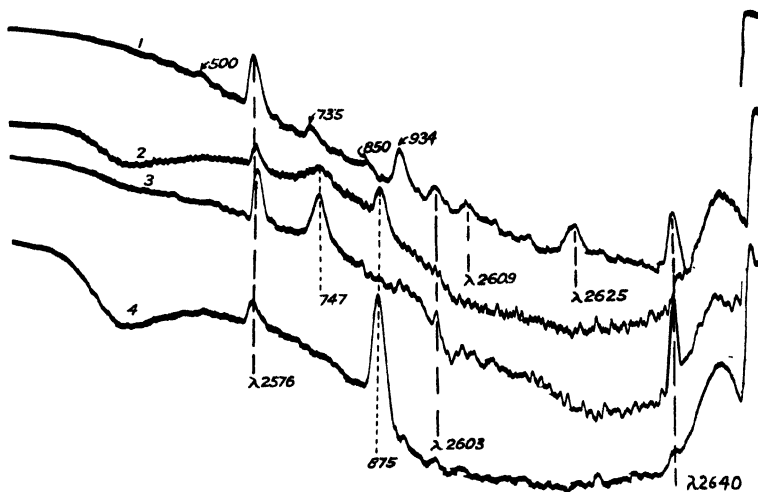
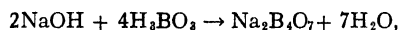
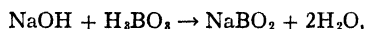


FIGURE 71. The Raman Spectra of Crystalline Sodium Tetraborate (Borax), Line 1, as Compared with its Solution, Line 2, Sodium Metaborate Solution, Line 3, and a Solution of Sodium Tetraborate to which has been added an Excess of Hydrochloric Acid, Line 4.

line tetraborate and metaborate. In Figure 70, line 1 represents the spectrum of aqueous boric acid solution. This microphotometer tracing shows the three strongest lines. The weakest ones were too feeble to register on the microphotometer but are visible on the original plates. The addition of a small proportion of sodium hydroxide to these solutions immediately diminishes the intensity of $\Delta\bar{\nu}$ 875 and produces a broad band whose maximum is at $\Delta\bar{\nu}$ 747. As sodium hydroxide is added, the $\Delta\bar{\nu}$ 875 progressively decreases and the 747 becomes less broad and increases in intensity. When the ratio of the boric acid molecules to sodium hydroxide molecules has the value of 2:1, or sufficient sodium hydroxide is added to convert all the boric acid to sodium tetraborate, according to the equation,



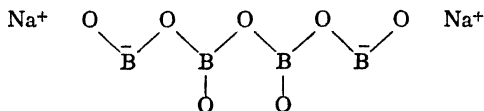
the intensities of these two lines are nearly equal, giving a spectrum which is comparable to that observed for the tetraborate. When the molecular ratios are 1:1, and sodium hydroxide has been added to form NaBO_2 , according to the equation,



the line at $\Delta\bar{\nu}$ 875 completely disappears. The addition of higher percentages of sodium hydroxide causes no further change in the principal line of the spectrum. The addition of an excess of hydrochloric acid to a solution of sodium tetraborate causes the disappearance of $\Delta\bar{\nu}$ 747, as shown in Figure 71, and the strengthening of 875, or in short, the reversion to boric acid.

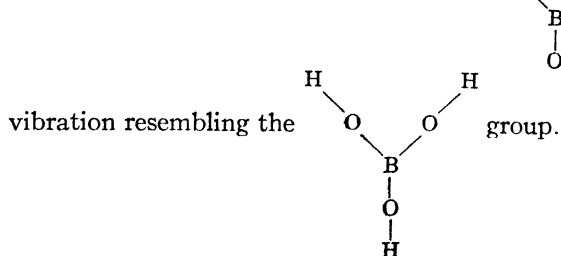
These results are best explained on the assumption that sodium metaborate, NaBO_2 , is produced initially by the addition of sodium hydroxide to boric acid. Consequently a mixture of boric acid and the metaborate is always present until one molecule of the base has been added for each molecule of the acid, at which time the conversion is complete. When sodium tetraborate is dissolved in water, it dissociates into $2\text{NaBO}_2 + 2\text{B}(\text{OH})_3$, where the NaBO_2 is ionized into Na^+ and BO_2^- ions. According to this conception, the tetraborate is completely, or nearly completely, dissociated in solution.

If the crystalline sodium tetraborate has the following chain formation:



then the two end groups $\left[\begin{array}{c} \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{B} \end{array} \right]^-$ would have a vibration similar to

sodium metaborate, and the intermediate $\text{O}-\text{B}-\text{O}^-$ groups should have a

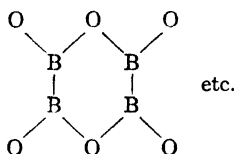


Sen and Gupta have investigated the infrared absorption spectra of the borates of lithium, potassium, calcium, magnesium, copper and lead. These authors conclude that the borate ion has a plane configuration which somewhat resembles the NO_3 and CO_3 ions. It is presumed from this analogy that they refer to the existence of a BO_3 ion. The origin of a BO_3 ion from the $\text{R}_2\text{B}_4\text{O}_7$ is not entirely clear. The nearest approach is the BO_3 group in the chain of the crystalline tetraborate as indicated above. The absorption frequencies observed by them in the infrared correspond to $\Delta\tilde{\nu}$ 709, 917, and 1315 (cf. Mitra's results). The fourth frequency calculated by them to be the inactive vibration, so far as infrared absorption is concerned, would fall at $\Delta\tilde{\nu}$ 1111. This vibration should correspond to the ν_1 type of oscillation or the symmetrical polarized frequency which appears most strongly in the Raman effect. This is obviously at $\Delta\tilde{\nu}$ 934, and it is difficult to correlate this result with the calculated $\Delta\tilde{\nu}$ 1111.

On taking up next the question of boric oxide as found in boric oxide glass, it can be seen that the observations of different observers are none too concordant. In Table 84, item 18 gives the observations of Langenberg.⁹⁴⁷ Item 19 includes the results of Avramenko.⁷⁶ Gross and Vuks,⁶⁶⁴ and Kujumzelis.⁹³¹ Of these frequency shifts, only $\Delta\tilde{\nu}$ 806 and 1260 were obtained by all the workers. Gross and Vuks record $\Delta\tilde{\nu}$ 1120 while Avramenko adds $\Delta\tilde{\nu}$ 602 and 1030. The only lines which may be ascribed to boric oxide with absolute certainty are, therefore, $\Delta\tilde{\nu}$ 806 and 1260. Item 20 refers to what Langenberg is pleased to call the BO_3 ion in glasses.

From the point of view of infrared absorption, one may consider, then, that there are two bands which have their counterpart in the Raman effect near $\Delta\tilde{\nu}$ 700 and 915, but that $\Delta\tilde{\nu}$ 1315, observed in the infrared, has no shift in the Raman effect near this region except 1261 or 1445. So far as considering a BO_3 -group in B_2O_3 as analogous to NO_3 , it should be pointed out that boric acid possesses the nearest known counterpart to a BO_3 -group, and that this acid has no Raman lines which correspond to those observed from the boric oxide glass.

Of course, several formulas may be set up to depict the structure of B_2O_3 . Among these is the following:



This has the objection, already raised, of probably yielding a Raman spectrum more complicated than the one observed. Other structures such as an asymmetric tetrahedron similar to that of phosphorus oxychloride would give rise to six Raman lines, while a linear one of the type A-B-A-B-A would yield but three frequency shifts. In the absence of polarization and reliable intensity data, it is impossible to assign accurately any specific structural configuration for boric oxide in boric oxide glass from the Raman spectra information. It can be shown, nevertheless, that a number of possible configurations are improbable.

In borax glass there is observed by Gross and Vuks⁶⁶⁴ a diffuse band from $\Delta\bar{\nu}$ 430–535, a very strong line at $\Delta\bar{\nu}$ 760, and three bands extending from 950–1000, 1077–1127, and 1310–1520. The maxima of these lines are in reasonable agreement with the results obtained from the crystalline sodium tetraborate with the possible exception of the frequency at $\Delta\bar{\nu}$ 934 which is much stronger than the one reported by Gross and Vuks for the same displacement. The lack of a frequency equivalent to $\Delta\bar{\nu}$ 875 as observed in solutions of boric acid containing sodium hydroxide, and the closer approach to the crystalline results, would apparently indicate a nearer relationship of the glass to crystalline borax than to the products formed in an aqueous solution of sodium tetraborate.

The results of these investigations indicate that boric acid is a molecule of the type AB_3 having the symmetry D_{3h} in which all the B groups lie at the corners of a plane triangle with the boron atom in the center. Crystalline boric acid has a spectrum which shows the presence of O—H linkages and the complete absence of any B—H linkage.

It had been supposed previously that the BO_2 ion in sodium metaborate corresponded to a linear group of the type A-B-A which would result in the appearance of only one Raman line. Since at least two lines have been observed, it would seem reasonable to conclude that the ion has a bent structure with the symmetry C_{2v} . There are no lines present in the solution of this compound which would correspond to a Na—B vibration thus indicating complete ionization. Proposed structures of this molecule based on a polymerized model or on a configuration resembling a benzene

ring are rejected on the ground that the simplicity of the Raman spectra is not in accord with such an interpretation.

The spectrum from sodium tetraborate indicates a dissociation of this compound into sodium metaborate and boric acid on solution. The addition of sodium hydroxide to boric acid apparently produces sodium metaborate in equilibrium with boric acid, and there is no compound comparable to crystalline sodium tetraborate in an aqueous solution. The addition of hydrochloric acid to a solution of sodium tetraborate results in the formation of boric acid. The stepwise conversion of boric acid to sodium metaborate in equilibrium with boric acid or the complete conversion to the metaborate is demonstrable by means of Raman spectra.

The spectrum of crystalline sodium tetraborate indicates that it is apparently nearly a composite of the spectra obtainable from BO_2 ions and from BO_3 groups. This is reasonably consistent with the supposition that sodium tetraborate is made up of long chains both in the crystalline and amorphous forms.

Several formulas have been proposed to depict the structure of B_2O_3 in glasses. From the data at hand it is not possible to designate which of the structures is correct, but it is possible to indicate that some of them are incorrect.

The Halogen Oxides of the Type XO , XO_2 and XO_3

Kujumzelis has obtained one Raman line for the spectrum of NaClO at $\Delta\bar{\nu}$ 713. After the solution had stood for five months two more lines appeared, $\Delta\bar{\nu}$ 802 and 935, the first being assigned to NaClO_2 and the last to the ClO_3 ion in view of the fact that a solution of gaseous ClO_3 exhibits a shift at $\Delta\bar{\nu}$ 935. In this category of compounds are included chlorates, bromates and iodates. Somewhat similarly constituted compounds such as the carbonates and the nitrates have been found to yield, respectively, as a rough average, $\Delta\bar{\nu}$ 710, 1050, 1450, and 725, 1050, and 1350 for the ν_2 , ν_1 and ν_3 types of vibration which correspond to the deformation, symmetrical and asymmetrical oscillations. The chlorates yield, according to Silveira,¹⁴³¹ Silveira and Bauer,¹⁴³⁵ Krishnamurti,⁹¹⁰ Daure,⁴⁵⁶ Schaefer, Matossi and Aderhold,¹⁴¹²⁻¹⁴¹⁵ Venkateswaran,¹⁶³⁹ Cabannes,³¹⁸ Shen, Yao and Wu,¹⁴²⁵ and Kujumzelis $\Delta\bar{\nu}$ 480, 615, 930, and 975, though these shifts have not all been observed by the above authors.

Notwithstanding the similarity between the CO_3 , NO_3 , and XO_3 ions there is a distinct difference. The first two of these were considered to have a planar structure having the symmetry D_{3h} which results in three fundamental Raman lines, while the XO_3 ion is presumed, particularly by Venkateswaran¹⁶³⁹ and Shen, Yao and Wu,¹⁴²⁵ to have the symmetry C_{3v} corresponding to a pyramidal structure. This structure yields four

fundamental Raman lines as noted above. From the polarization measurements of the latter authors it is evident that in halogen compounds of the type ClO_3 , $\Delta\bar{\nu}$ 930 ($\rho = 0.35$), 615 ($\rho = 0.56$), 975 ($\rho = 0.87$) and 480 ($\rho = 0.90$) correspond to the two parallel and two perpendicular vibrations respectively, of which the last two are doubly degenerate. These are designated by Venkateswaran as ν_1 and ν_2 (the high and low vibrations parallel to the figure axis) and ν_3 and ν_4 (the high and low perpendicular vibrations). The notation which has been generally used in this treatment for this type of molecule is that ν_1 and ν_3 represent the high and low parallel and ν_2 and ν_4 the perpendicular displacements. It is the latter system which will be continued here for the sake of uniformity. The halogen oxides of the type XO_3 may thus be considered both individually and collectively.

The magnitude and the intensities of the shifts from these compounds are shown in Table 85 (cf. Table 72).

The degree of depolarization for some of the chlorates has already been referred to. For the bromates and iodates the ν_1 and ν_4 types of oscillation yield the depolarization factors $\rho = 0.38, 0.89$ and $0.43, 0.81$, respectively, together with 0.67 for the ν_2 oscillation in the iodates.¹⁴²⁵

It is apparent from this table that in the crystalline state it is the degenerate vibrations which are partially split into their components. This is principally true of the bromates and iodates. The ν_4 oscillation in crystalline potassium bromate for example, yields $\Delta\bar{\nu}$ 333 and 357 and the ν_2 oscillation possibly results in $\Delta\bar{\nu}$ 813 and 830, although the first of these shifts may be more related to $\Delta\bar{\nu}$ 795, the ν_1 type of vibration. This is because $\Delta\bar{\nu}$ 795 lies almost exactly half way between $\Delta\bar{\nu}$ 778 and 813. Any combination of vibrations which would produce resonance phenomena, however, would probably be present in the liquid as well as the solid state. This explanation is not too satisfactory. Venkateswaran attributes this splitting to "positional degeneracy." The complete separation of these lines is possible only in the crystalline state.

The angle of the pyramid for all these three halogen compounds is approximately 55° . The symmetrical valence oscillation varies from $\Delta\bar{\nu}$ 930 in the chlorates to 806 and 796 in the bromates and iodates. This diminution between the bromates and iodates is actually relatively small, notwithstanding the contention of Venkateswaran that there is a progressive decrease of this frequency in these halogen compounds. It is apparent from the published data, particularly those based on the results from solutions where degenerate splitting does not play so important a role, that the alteration of the ν_1 vibration is less between the bromates and iodates than between the chlorates and bromates.

Table 85.—The Raman Shifts of Some Oxygen Halides.

Compounds	Raman Shifts				
	125(3)	177(1)	376(7)	490(1) 480(3) 478(3) 478(4)	533
NaClO ₂ (cryst.)					
NaClO ₂ (sol.)					
KClO ₂ (cryst.)	125(3)	177(1)			493(0)
KClO ₂ (sol.)					
Mg(ClO ₂) ₂ (sol.)					
Ba(ClO ₂) ₂ (cryst.)					
NaBrO ₂ (cryst.)					
NaBrO ₂ (sol.)			357(2)	457(1)	
KBrO ₂ (cryst.)			350(3)	461(0)	
KBrO ₂ (sol.)			357(2)	452(0)	
Mg(BrO ₂) ₂ (cryst.)			368(1)		
Cd(BrO ₂) ₂ (cryst.)					
LiIO ₃ (cryst.)	169(1)	245(5)		459(0)	
LiIO ₃ (sol.)				423(0)	
NaIO ₃ (cryst.)					
NaIO ₃ (sol.)	132(0)	229(0)	341(1)		
KIO ₃ (cryst.)			333(1)		
KIO ₃ (sol.)			333(1)		
NaClO ₃ (cryst.)	620(0)			905(2)	930(5)
NaClO ₃ (sol.)	611(3)			928(10)	975(0)
KClO ₃ (cryst.)	620(1)			915(1)	930(10)
KClO ₃ (sol.)				930(10)	977(1)
Mg(ClO ₃) ₂ (sol.)	604			930	
Ba(ClO ₃) ₂ (cryst.)	612(0)			913(1)	930(8)
NaBrO ₃ (cryst.)					
NaBrO ₃ (sol.)			842(3)		
KBrO ₃ (cryst.)					
KBrO ₃ (sol.)		778(3)	832(2)		
Mg(BrO ₃) ₂ (cryst.)		789(0)			
Cd(BrO ₃) ₂ (cryst.)		785			
LiIO ₃ (cryst.)	608(0)	765(10)	813(1)	822(0)	
LiIO ₃ (sol.)	603(0)			806(10)	
NaIO ₃ (cryst.)		738(6)	809(5)	813(1)	
NaIO ₃ (sol.)		720(0)			
KIO ₃ (cryst.)		737(8)	789(5)	796(6)	
KIO ₃ (sol.)					
KIO ₃ (sol.)					

Miscellaneous Oxides

Most of these oxides are of the type XO_4 . This type is encountered also in the sections devoted to the phosphates, periodates, perchlorates, sulfates and silicates. The symmetry of the XO_4 group is generally tetrahedral, resulting therefore in the usual four fundamental lines, two of which are triply degenerate and one doubly degenerate, while the remaining one corresponds to the symmetrical oscillation. The high and low symmetric and deformation oscillations are designated ν_1 , and ν_2 , ν_3 and ν_4 respectively, according to the system which has been employed thus far in compounds of this type.

To the group from phosphates to silicates, named above, which behave in a normal manner may be added the chromates and possibly the arsenates. There is not sufficient information available to determine the precise type of vibrations of the vanadate and permanganate ions.

While in some cases four frequencies have been observed from the tungstate and molybdate ions, at least one of these lines is extremely weak. Furthermore, with all other oxides it is the ν_3 vibration which has the largest magnitude and not the ν_1 type. If the magnitudes of the symmetrical vibrations of all the oxides are plotted against the square root of the molecular weight they will fall roughly on a straight line, with the exception of the oxides of molybdenum and tungsten. Nisi¹¹⁷⁵ indicated early that the ν_1 Raman shifts of the oxygen derivatives of sulfur, selenium and tellurium decrease with an increasing atomic number of the central atom, and that those of molybdenum and tungsten increase. In any case Venkateswaran¹⁶³⁹ places the ν_1 oscillation for the tungstates and molybdates as the largest frequency observed, in contradistinction to its relative magnitude in other compounds of this variety. Gupta⁶⁷⁹ considers these compounds as octahedral rather than tetrahedral. This point of view is disputed by Venkateswaran.

Theodoresco¹⁵⁵⁵ points out the general similarity between the molybdate ion and the sulfate ion. This is a matter of relativity. Molybdic acid produces a triplet line $\Delta\tilde{\nu}$ 853(2), 901(6) and 950(10), a band from 216–365 containing some lines of indeterminate magnitude, and a possible band near $\Delta\tilde{\nu}$ 435. The complex molybdate gives different spectra from those of the simple compounds.

So far as the arsenates are concerned, Fehér and Morgenstern⁵⁴⁴ have indicated in a brief study of these compounds that different pairs of lines which are influenced by deuterium substitution in tri-, di-, and mono-substituted compounds. The pairs $\Delta\tilde{\nu}$ 770 and 760, 870 and 863, 701 and 693 are affected primarily. This demonstrates the effect of the residual hydrogen influence and is particularly significant in the interpretation of the spectra of the phosphoric acid derivatives. All these results are

Table 86.—The Raman Shifts from Miscellaneous Oxides.

$\text{Na}_2\text{WO}_4(\text{sol.})$		325(2)	452(0)		
$\text{Na}_2\text{WO}_4(\text{alkaline sol.})$		320(3)			
$\text{Na}_2\text{WO}_4(\text{cryst.})$					
$\text{K}_2\text{WO}_4(\text{alkaline sol.})$		320(3)			
CaWO_4					
$(\text{NH}_4)_2\text{MoO}_4(\text{cryst.})$	223	362(1)			
$(\text{NH}_4)_2\text{MoO}_4(\text{sol.})$	216(3)	360(2)			
$(\text{NH}_4)_2\text{MoO}_4(\text{ammonia sol.})$		326(3)			
$\text{K}_2\text{MoO}_4(\text{alkaline sol.})$		319(8)			
$\text{Na}_2\text{MoO}_4(\text{sol.})$	241(0)	320(3)			
PbMoO_4					
$\text{KMnO}_4(\text{sol.})$					
$\text{Na}_2\text{CrO}_4(\text{cryst.})$		491(1)	504(0)		
$\text{Na}_2\text{CrO}_4(\text{sol.})$		481(2)	503(1)		
$\text{K}_2\text{CrO}_4(\text{sol.})$		486(3)	513(1)		787
$\text{K}_2\text{CrO}_4(\text{cryst.})$		486(1)	513(0)		
$(\text{NH}_4)_2\text{CrO}_4(\text{sol.})$		483(0)			
H_3AsO_4 (88.5%)	265	325	388		770
D_3AsO_4 (86.5%)	265	325	388		760
NaH_2AsO_4		295	360		744
NaD_2AsO_4		295	360		744
Na_2HAsO_4		323	386		701
Na_2DAsO_4		323	386		693
Na_3AsO_4		349(1)	462(2)		
$\text{Na}_3\text{VO}_4(\text{sol.})$					
Na_2AsO_3	144(1)	203(1)			
NaVO_3		228(1)	367(1)		
$\text{H}_6\text{TeO}_6(\text{sol.})$		333(3)		619(1)	644(10)
$\text{H}_7\text{TeO}_6 \cdot 2\text{H}_2\text{O}$		365(2)			657(0)
H_2TeO_4		357(3)		624(1)	647(10)
$\text{Na}_2\text{WO}_4(\text{sol.})$	840(2)			930(7)	1017(1)
$\text{Na}_2\text{WO}_4(\text{alkaline sol.})$	834(1)			929(4)	1394(1)
$\text{Na}_2\text{WO}_4(\text{cryst.})$				928(8)	1540(2)
$\text{K}_2\text{WO}_4(\text{alkaline sol.})$	835(1)			930(5)	
CaWO_4				928	
$(\text{NH}_4)_2\text{MoO}_4(\text{cryst.})$		891(4)	915(1)	936(7)	
$(\text{NH}_4)_2\text{MoO}_4(\text{sol.})$		890(4)		944(10)	
$(\text{NH}_4)_2\text{MoO}_4(\text{ammonia sol.})$	820(2)	895(5)			
$\text{K}_2\text{MoO}_4(\text{alkaline sol.})$	823(3)	891(10)			
$\text{Na}_2\text{MoO}_4(\text{sol.})$	845(2)	898(8)			
PbMoO_4				932	
$\text{KMnO}_4(\text{sol.})$	833	888			
$\text{Na}_2\text{CrO}_4(\text{cryst.})$	859(7)	863(1)			
$\text{Na}_2\text{CrO}_4(\text{sol.})$	855(4)	874(0)			
$\text{K}_2\text{CrO}_4(\text{sol.})$	852(10)	879(1)			
$\text{K}_2\text{CrO}_4(\text{cryst.})$	859(6)	877(0)			
$(\text{NH}_4)_2\text{CrO}_4(\text{sol.})$	838(5)				
H_3AsO_4 (88.5%)	815	867	919		
D_3AsO_4 (86.5%)	815	867	919		
NaH_2AsO_4	833	870	908		
NaD_2AsO_4	833	863	908		
Na_2HAsO_4		836			
Na_2DAsO_4		838			
Na_3AsO_4		837(3)			
$\text{Na}_3\text{VO}_4(\text{sol.})$		876(2)	907(1)		
Na_2AsO_3					
NaVO_3					
$\text{H}_6\text{TeO}_6(\text{sol.})$					
$\text{H}_7\text{TeO}_6 \cdot 2\text{H}_2\text{O}$					3121
H_2TeO_4					

indicated in Table 86, made chiefly from the observations of Nisi,¹¹⁷⁵ Gupta,⁶⁷⁹ Krishnamurti,⁹¹⁰ Damaschun,⁴⁵¹ Ghosh and Das,⁴⁸¹ Theodoresco,¹⁵⁵⁵ Fehér and Morgenstern,⁵⁴⁴ and Venkateswaran.¹⁶³⁹ One can

speculate, of course, on the significance of the arsenic oxide results. The shifts would be expected to follow the general pattern in relation to the type of vibration, and the magnitude of the shifts would vary from low to high according to the following scheme ν_2 , ν_4 , ν_1 and ν_3 , (or ν_2 , ν_4 , ν_3 and ν_1 cf. MoO_4) for a tetrahedral model. Some of the frequencies appearing below $\Delta\bar{\nu}$ 800 should represent a splitting of the ν_2 and ν_4 type of vibration. The same statement may be made regarding those frequencies in excess of $\Delta\bar{\nu}$ 850, but without polarization and intensity measurements it is purely a matter of opinion as to which lines represent specific types of vibration.

Other arsenic compounds also studied by Fehér and Morgenstern,⁵⁴⁴ which illustrate in a minor degree the effect of substitution in molecules of the type XO_4 , XO_3B , XO_2B_2 , etc., are indicated in Table 87. An inter-

Table 87.—The Raman Shifts from Some Arsenic Oxides and Derivatives.

Compounds	Raman Shifts						
Na_2AsO_4		342	398				810
$\text{Na}_2\text{AsO}_3\text{S}$			370	394	446	741	800
$\text{Na}_2\text{AsO}_3\text{S}_2$			360	382	432	470	800
Na_2AsOS_3			365		416	465	800
Na_2AsS_4				386	419		
Na_2SbS_4	171	216		366	380		
$\text{Na}_2\text{AsO}_3\text{Se}$	156	178	289	361	410		496

pretation of these results is made difficult by the incompleteness of the spectra and the lack of intensities and polarization determinations. Nevertheless the results are intrinsically interesting. The total number of Raman lines does not correspond to that expected from molecules of the type represented, unless there is an overlapping of specific frequencies which is unlikely. Those lines which apparently are missing will probably be found on further investigation.

Telluric acid ¹⁶³⁹ gives rise to three principal lines $\Delta\bar{\nu}$ 647(10) (P), 624(1) (D), 357(3) (D); of these the first is possibly the symmetrical ν_1 vibration, and the others are the ν_2 doubly degenerate and the ν_3 triply degenerate vibrations obtainable from a molecule of an octahedral symmetry. This indicates a molecule of the type $\text{Te}(\text{OH})_6$ rather than $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$. This is satisfactorily confirmed by the absence of any $\text{O} \leftrightarrow \text{H}$ frequency other than $\Delta\bar{\nu}$ 3121 which may possibly be too low to be attributed to water of crystallization and is more characteristic of the $\text{O}-\text{H}$ involved in hydrogen bonding.

The individual differences between such closely related compounds as sodium arsenite and sodium arsenate are strikingly marked. The progressive change from *meta*- to *ortho*-vanadate structure has been noted by Ghosh and Das.⁴⁸¹

Nitrates

The Raman spectrum of the nitrates consists almost exclusively of the spectrum of the NO_3 -group. In consequence of this the spectrum is not

Table 88.—The Raman Shifts from Nitrates.

Compounds	Raman Shifts									
LiNO_3				100(2)		189(4)				
NaNO_3										
KNO_3	31(0)	51(4)	84(8)							
RbNO_3				109(2)	147					
CsNO_3				116(1)	149(?)					
NH_4NO_3		59(1)	86(1)		142(2)	170(1)				
$\text{Cu}(\text{NO}_3)_2$							279		442	
AgNO_3										
$\text{Ba}(\text{NO}_3)_2$										
$\text{Sr}(\text{NO}_3)_2$										
$\text{Ca}(\text{NO}_3)_2$										
$\text{Be}(\text{NO}_3)_2$										
$\text{Mg}(\text{NO}_3)_2$										
$\text{Zn}(\text{NO}_3)_2$										
$\text{Cd}(\text{NO}_3)_2$										
HgNO_3					169(3)					
$\text{Hg}(\text{NO}_3)_2$										
$\text{Pb}(\text{NO}_3)_2$					155(0)					
$\text{Mn}(\text{NO}_3)_2$										
$\text{Al}(\text{NO}_3)_3$							396(1)	446(0)	537(1)	627(0)
$\text{Bi}(\text{NO}_3)_3$										
$\text{La}(\text{NO}_3)_3$										
$\text{Ce}(\text{NO}_3)_3$										
TiNO_3										
$\text{Th}(\text{NO}_3)_4$										
LiNO_3	725(2)			1063(6)			1390(2)			
NaNO_3	720(1)			1055(5)			1381(1)	1414(1)		
KNO_3	713(2)			1048(7)		1348(1)		1413(2)		
RbNO_3	706(0)			1055(6)		1354(0)				
CsNO_3	715(1)			1050(6)		1346(0)				
NH_4NO_3	718(1)			1044(6)		1332(1)	1372(2)	1400(1)		
$\text{Cu}(\text{NO}_3)_2$	717(2)	754(1)		1048(3)		1325(1)		1421(0)	1476(1)	
AgNO_3	713(2)			1042(4)		1366(1)				
$\text{Ba}(\text{NO}_3)_2$	728(2)			1047(6)		1363(2)				
$\text{Sr}(\text{NO}_3)_2$	725(2)			1054(6)		1354(0)				
$\text{Ca}(\text{NO}_3)_2$	715(2)	740(2)		1064		1353		1444		
$\text{Be}(\text{NO}_3)_2$				1049(6)						
$\text{Mg}(\text{NO}_3)_2$	726(2)			1053(4)		1346(1)		1427		
$\text{Zn}(\text{NO}_3)_2$	726(1)			1045(2)						
$\text{Cd}(\text{NO}_3)_2$	714(1)	730(2)		1051(6)		1364(2)				
$\text{Hg}(\text{NO}_3)_2$	730(2)			1053(6)			1377(2)			
$\text{Hg}(\text{NO}_3)_2$	706(0)	741(0)		1037(6)						
$\text{Pb}(\text{NO}_3)_2$	727(2)			1046(3)						
$\text{Mn}(\text{NO}_3)_2$	716(1)			1036(2)			1391(1)			
$\text{Al}(\text{NO}_3)_3$	714(1)	746(1)		1052(2)	1241(0)	1318(2)		1414(2)		
$\text{Bi}(\text{NO}_3)_3$	730(1)		980(0)	1036(4)				1417(1)		
$\text{La}(\text{NO}_3)_3$	714(1)	740(3)		1032(6)				1416		
$\text{Ce}(\text{NO}_3)_3$	712(1)	740(1)		1046(6)			1396		1475	
TiNO_3				1042(3)						
$\text{Th}(\text{NO}_3)_4$	712(1)	746(1)		1038						

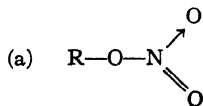
Note: No lines due to the ammonium group are included in this table.

materially altered by changes in the state of aggregation. It has been generally believed that the configuration of the nitrate ion is a plane equilateral triangle having the symmetry D_{3h} . The nitrogen atom is situated in the center of the triangle. This group should have six fundamental frequencies. However, for reasons of symmetry these would be reduced to four, as two of the frequencies are doubly degenerate. Only three shifts, however, are actually observed; the fourth is inactive in the Raman spectrum and appears in the infrared absorption. The three principal frequencies occur near $\Delta\bar{\nu}$ 720, 1050, and 1350. These are shown in Table 88. In several cases the complete spectrum has not been determined.

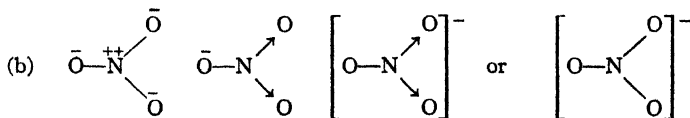
This table makes no differentiation in the state of aggregation and represents a composite picture of the nitrates of various elements. While there are differences in the magnitude of these three principal shifts resulting from the influence of the cation, the variations are not always so great as this table indicates. This is because intercomparison of the results obtained by different observers is not usually more accurate than 10 wave numbers. However, when a particular observer has measured a series of nitrates under identical conditions, small changes in the magnitude of these shifts are probably significant. With the possible exception of aluminum nitrate the shifts which appear below $\Delta\bar{\nu}$ 700 occur only in the crystalline form and may be attributed to a vibration originating in the crystal lattice. The frequency appearing at approximately $\Delta\bar{\nu}$ 1450 has been accounted for as a combination of $2\nu_4$. Both ν_3 and ν_4 should be depolarized, as these shifts are doubly degenerate. On the other hand, ν_1 which corresponds to the symmetrical expansion and contraction of the triangle, is polarized.

It will be noticed in Table 88 that with some cations there is a splitting of a frequency at $\Delta\bar{\nu}$ 720 and possibly at $\Delta\bar{\nu}$ 1350 into two components. This is due apparently to a deformation of the nitrate group by the cation. These frequencies are then no longer completely doubly degenerate as a result of the induced asymmetry.

It may be superfluous to mention that the nitrate ion can in no wise be considered as directly related to the organic nitrates. These have the structure



while the nitrate ion may be represented by



which are different ways of expressing the same net result. The methods of arriving at this result may be different.

The distinction between the nitrate ion and the organic nitrates is particularly evidenced by the absence of the frequency shift in the $\Delta\bar{\nu}$ 1650 region in the Raman spectrum of the former. This shift, as has been pointed out in the discussion of the constitution of organic nitrates and nitric acid, is present in these compounds and represents the N=O group.

Returning more specifically to a consideration of the possible influence of the state of aggregation and the cations present on the magnitude of the frequency shifts, it may be said that at the present time this is a matter of opinion. Ollano and Frongia¹¹⁹² maintain that the univalent salts particularly possess lines near $\Delta\bar{\nu}$ 720 and 1440, which are single lines. These lines are very wide, and probably double in the divalent salts and are clearly doublets in the trivalent compounds. I. R. Rao,^{1312, 1314} on the other hand, maintains that in solution the shifts are $\Delta\bar{\nu}$ 725, 1049, 1357, more or less independent of the cation. Likewise there is a distinct lowering of the magnitudes of the shifts in going from the crystalline to the molten or fluid states. This decrease may amount to 20 wave numbers. He reports a frequency near 1670 in the crystals.

A change in the frequencies of the nitrate group as a function of physical state is partially substantiated by the work of Thatte and Ganesan^{1545, 1547} who find, for example, the following changes in a number of the nitrates investigated as shown in Table 89. The spectrum is not complete in every

Table 89.—The Raman Shifts from Nitrates in Different States of Aggregation.

Compounds	Raman Shifts							
	Fused			Crystal			Solution	
LiNO ₃		1060		728	1069	1391	1050	
NaNO ₃	715	1054	1393	720	1066	1383	725	1048 1361
KNO ₃	721	1052	1343	711	1051	1350	730	1049 1357
AgNO ₃		1038	1360		1045	1372		1042
Mg(NO ₃) ₂	720-750	1052	1372		1059			1048
Zn(NO ₃) ₂	725-740	1041			1044			1049
Cd(NO ₃) ₂	730	1046						1047
Al(NO ₃) ₃	740-790	1049	1320		1058			
TiNO ₃		1038						

case. From this work it is concluded that in solution the structure and dimensions of the nitrate ion are the same regardless of the cation. In the crystalline compounds, however, it has been shown from x-ray investigations that the dimensions of the NO₃-group vary with different nitrates. In other words, in lithium nitrate the N—O distance is less than in sodium nitrate. The fused nitrates lie about halfway between the crystals and solution in the magnitude of their frequency shifts. Two sharp, low frequency shifts have been noted by Nedungadi (Raman Jubilee volume) namely, $\Delta\bar{\nu}$ 98 and 185 from crystalline sodium nitrate. The magnitudes

of these shifts are displaced to a lower value as the temperature is increased, and on melting the shifts are replaced by a broad wing extending on both sides of the exciting line. (Note also recent work of Raman and Nedun-gadi.)

Costeanu⁸⁸⁸ has noticed a very feeble displacement of the symmetrical oscillation near $\Delta\bar{\nu}$ 1045 toward shorter wave numbers in liquid ammonia. In solutions there is apparently no alteration in the principal shift at different concentrations according to Sterling and Laird.¹⁵⁰⁴ More recently, however, Laird and Plesset have confirmed the observations of Grassman that this frequency diminishes with increasing concentration in lead and silver nitrate solutions and is little affected in cadmium nitrate solutions. In solution there never has been any evidence of a homopolar linkage between the cation and the nitrate group irrespective of concentration.¹⁴⁴⁶

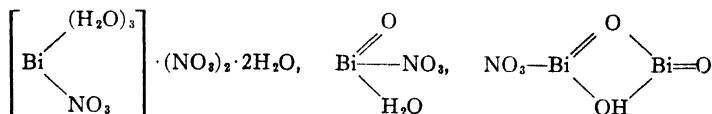
Grassmann^{638, 639, 640} and Silveira,^{1433, 1434} as well as others, particularly noted the splitting of the $\Delta\bar{\nu}$ 720 and 1350 frequencies in calcium and copper salts. The ratio of the intensities of the $\Delta\bar{\nu}$ 720 components, namely, $\Delta\bar{\nu}$ 715 and 740 for calcium nitrate, varies according to the concentration, from the results of Bauer, Magat and da Silveira.¹⁰⁸ In the more concentrated solutions $\Delta\bar{\nu}$ 740 is stronger than $\Delta\bar{\nu}$ 715, but in dilute solutions the intensities are reversed. Woodward¹⁷³² finds some evidence for an Hg—Hg shift in a saturated solution of mercurous nitrate. This is because of a line appearing at $\Delta\bar{\nu}$ 169. In thallium nitrate there is likewise a Th—Th binding. The amount of this compound present is less than ten per cent. Pattabhiramayya,¹²¹¹ in an exhaustive study of a sodium nitrate crystal, confirms the two lattice vibrations near $\Delta\bar{\nu}$ 100 and 186 and the interpretation that the ν_1 , ν_3 and ν_4 vibrations are respectively 1069, 1388 and 727, with the ν_2 vibration, active only in the infrared, as $\Delta\bar{\nu}$ 830. In addition there is observed $\Delta\bar{\nu}$ 1669 which is best explained as a harmonic of ν_2 . The appearance of harmonics of ν_2 in the Raman effect, while the fundamental is lacking, is not unusual and occurs in other molecules of this type. The nitrogen atom, in this case, oscillates along the symmetry axis, and it is easily seen that the polarizability ellipsoid is deformed with a frequency double that of the molecule.

The ordinary vibrations are slightly affected by a temperature increase, and the lattice vibrations are, as is to be expected, more strongly altered. With an elevated temperature $\Delta\bar{\nu}$ 189 is markedly diminished in intensity. In aqueous solution the lattice vibrations are absent. In crystals the ν_3 vibration increases in intensity at the expense of the ν_4 type but in solution the conditions are reversed.

From this it may be concluded that in crystals there are forces which restrict one mode of oscillation in preference to another.

It is presumed by Ollano¹¹⁹⁰ that bismuth nitrate hydrolyzes in the

presence of nitric acid to compounds to which he assigns the following structures:



The nitrate ion is in part ionized and in part attached directly to bismuth. It is postulated that aqueous nitric acid solutions of bismuth nitrate contain NO_3^- , Bi^{+++} , BiOH^{++} , and $\text{Bi}(\text{OH})_2^+$. With diminishing concentration of the acid the concentration of the bismuth ions and BiOH^{++} decreases, while that of $\text{Bi}(\text{OH})_2^+$ increases. The spectrograms give, in addition to the lines attributable to the nitrate ions, $\Delta\bar{\nu}$ 3595, 1600, and 1500. Of these shifts, $\Delta\bar{\nu}$ 1600 at the lower concentrations has a medium intensity, and $\Delta\bar{\nu}$ 1500 always appears intense and sharp. The last two frequencies are assigned to the $\text{Bi}(\text{OH})_2^{++}$ and BiOH^{++} groups, respectively. The frequency $\Delta\bar{\nu}$ 3595 is assigned to the $\text{H} \leftrightarrow \text{O}$ vibration. The $\Delta\bar{\nu}$ 1236 is without assignment.

These allocations of wave number shifts to these specific molecular structures are admittedly somewhat arbitrary in view of the scant experimental data upon which they are predicated. It is probable that $\Delta\bar{\nu}$ 1600 and 3600 can be assigned to the oscillations in the water molecules, as is discussed under the Raman spectrum of water.

One other interesting application of Raman spectra to the study of nitrates might be mentioned. In the solid state the Raman spectrum from the solid eutectic of sodium nitrate and potassium nitrate shows only one sharp principal frequency for the nitrate group when freshly prepared, according to Gerlach.⁵⁹⁶ After a period of approximately one day, however, the initially sharp line becomes gradually broad and diffuse, finally separating with increasing time into two sharp distinct lines. One of these has a frequency shift corresponding to that of sodium nitrate and the other to potassium nitrate. The initial sharp line obtained from the eutectic lies halfway between the two final lines attributed to sodium nitrate and potassium nitrate, respectively. X-ray diffraction patterns show no difference between samples at different ages, and the results are independent of the rate of cooling. It might be mentioned, however, that KNO_3I first changes metastably to KNO_3III , which then inverts to KNO_3II , according to Kracek. Whether or not this has any connection with the suppositions of Gerlach is a matter for further investigation.

Nitrites

Crystalline sodium nitrite is reported by Carrelli, Pringsheim, and Rosen⁸⁴⁴ to yield $\Delta\bar{\nu}$ 696, 785, and 1303. Bär⁸⁹ concurs in only $\Delta\bar{\nu}$ 1333.

Ghosh and Das⁵⁹⁸ report the same frequencies in solution as observed by Carrelli, Pringsheim, and Rosen in crystals. Brunetti and Ollano²⁹⁴ report $\Delta\bar{\nu}$ 815, 1291, and 1326 in solution. Dadieu and Kohlrausch⁸¹⁹ report for potassium, calcium, and barium nitrites a number of frequencies whose averages are: $\Delta\bar{\nu}$ 588(2), 660(2), 714(2), 815(2), 1231(1), and 1325(5). There is a notable lack of agreement between these observations. More recently Langseth and Walles⁹⁶⁷ have carefully redetermined the spectrum obtainable from sodium nitrite. These authors observed $\Delta\bar{\nu}$ 813, 1220, and 1331, in agreement with the results of Brunetti and Ollano already referred to. The relative intensities of these lines are (1), (3), and (10), respectively. These relative intensities do not change between 15° C. and 95° C. The depolarization factors, ρ , for these three lines are, respectively, 0.21, 0.84, and 0.43. This is in agreement with the concept that the nitrite ion has a symmetry C_{2v} and should give rise to three Raman lines: ν_1 the polarized and symmetrical vibration corresponding to $\Delta\bar{\nu}$ 1331, ν_2 the symmetrical and polarized vibration corresponding to the deformation vibration $\Delta\bar{\nu}$ 813, and last of all ν_3 the asymmetrical vibration exemplified by $\Delta\bar{\nu}$ 1240. It is to be noted in this case that the ν_1 vibration is of larger magnitude than the asymmetrical one ν_3 . This is in contradistinction to the ratio of these two frequencies in sulfur dioxide or in water.

As the nitrite ion possesses but three fundamental frequencies there are no degenerate vibrations; consequently the frequencies observed by Kohlrausch⁸¹⁹ between $\Delta\bar{\nu}$ 590 and 710 remain unexplained. It is probable that these are erroneous. It should be mentioned that the nitrite group in methyl nitrite possesses a Raman shift at $\Delta\bar{\nu}$ 1648. Furthermore, the organic nitro- compounds, as represented by nitromethane and tetranitromethane, possess a frequency near $\Delta\bar{\nu}$ 1600. No such frequency is observed in the inorganic nitrite ion. The organic nitro- compounds, however, do possess a shift near $\Delta\bar{\nu}$ 1340 to 1360, which may be somewhat analogous to the $\Delta\bar{\nu}$ 1330 observed in sodium nitrite. This cannot be ascribed to a carbon-hydrogen vibration as it is present in tetranitromethane.

Azides

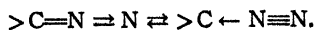
According to Petrikaln and Hochberg^{1222, 1223} the aqueous solution of sodium azide yields one Raman frequency, namely, $\Delta\bar{\nu}$ 1221. In the more careful investigations of Langseth, Nielsen and Sorensen⁹⁶⁵ there are present two Raman frequencies $\Delta\bar{\nu}$ 1348 and 1258, whose intensity ratios are respectively 100 to 1. The polarization constant of $\Delta\bar{\nu}$ 1348 is 0.16. From these data it would seem probable that the strongest frequency represents a ν_1 symmetrical vibration. In the infrared absorption $\Delta\bar{\nu}$ 2040 is observed. From this viewpoint the azide ion is probably analogous to the CO_2 group

having the symmetry $D_{\infty h}$. This should give rise to but one observable Raman line. The presence of two lines is explained on the basis that $\Delta\tilde{\nu}$ 1258 is an overtone of a frequency appearing near $\Delta\tilde{\nu}$ 629. This would lead to the conclusion that the azide ion has the following linear structure: $\bar{N}=\overset{+}{N}=\bar{N}$.

However, there is another possibility based on the recent observations of Venkateswaran¹⁶³⁹ and Engler and Kohlrausch.⁵⁵³ This is that the structure of the azide ion may be linear and unsymmetrical and may have the configuration $N=N\equiv N$, somewhat akin to the form $O=N\equiv N$ sometimes used for nitrous oxide. These two forms, however, do not represent a static configuration but rather an effective structure derived from the resonance between $O-N\equiv N$ and $O=N\equiv N$. Assuming this to be true one form of the azide ion could be represented by $[\bar{N}-\overset{+}{N}\equiv\bar{N}]$. This would have the symmetry $C_{\infty h}$ according to which all the Raman frequencies should be active. Venkateswaran in particular has observed three such frequencies from solid sodium azide, namely $\Delta\tilde{\nu}$ 636(0), 1267(2), 1356(10) and 2077(0), and in solution $\Delta\tilde{\nu}$ 1260(2), 1346(10) and 2066(0). Here $\Delta\tilde{\nu}$ 1267 is again considered to be an overtone of $\Delta\tilde{\nu}$ 636. The deformation oscillation ν_2 is therefore $\Delta\tilde{\nu}$ 636. The symmetrical valence oscillation ν_1 is 1346, while the asymmetric ν_s vibration corresponds to $\Delta\nu$ 2066. Venkateswaran considers that the linear and unsymmetrical form should be written as $N\equiv N=\overset{+}{N}$, but for the reasons given above the resonance formula would seem to be more probable.

Engler and Kohlrausch⁵⁵³ write the configuration of hydrazoic acid as $H-N\equiv N$. This leads to the same pentavalent concept of a nitrogen atom, which is unlikely. More probably there is resonance between $R-\bar{N}-\overset{+}{N}\equiv N$ and $R-\overset{+}{N}\equiv N-\bar{N}$. In liquid hydrazoic acid $\Delta\tilde{\nu}$ 1300(5) and 2389(1) were observed, but this spectrum is doubtless incomplete. The $C\equiv N$ shift in the acid is much higher than in the salts. The frequency $\Delta\tilde{\nu}$ 2066 is quite consistent with the values observed in potassium cyanide and hydrogen cyanide. The shift at $\Delta\tilde{\nu}$ 2389 has no counterpart among inorganic cyanides except dicyanine. No shift is observed for a $H-N$ linkage in the frequency region near $\Delta\tilde{\nu}$ 3200. The unsymmetrical arrangement of these molecules is confirmed by electron diffraction measurements. In compounds of the type $R-\overset{+}{N}\equiv\bar{N}-\bar{N}$ the R group is at an angle to the axis passing through the nitrogen atoms.

This type of resonance hybrid also has been observed among the diazo-compounds where the structures are represented by



Chapter 28

The Raman Spectra of Cyano- and Complex Compounds

The organic derivatives of the compounds considered in this chapter have been discussed in the chapter on cyano- compounds, thiocyanates and isocyanates. The simplest of the inorganic compounds is hydrogen cyanide, for which Dadieu^{397, 402} obtained $\Delta\tilde{\nu}$ 2062 and 2094 and for which Bhagavantam¹³⁵ observed $\Delta\tilde{\nu}$ 2076, 2097 and 2122. Dadieu attributed the $\Delta\tilde{\nu}$ 2062 shift to the isomer HNC. This simple explanation is open to some question. In organic molecules the $\text{C}\equiv\text{N}$ linkage is approximately 2245. On the other hand the isonitriles, which may be more or less characterized by $\text{R}-\text{C}\equiv\text{N}$, yield two frequencies corresponding to approximately $\Delta\tilde{\nu}$ 2146 and 2161, both of which are of nearly the same intensity. In the nitriles or the isonitriles these frequencies are in the region which has been ascribed to the triple bond. It can be assumed, therefore, that all of these compounds involve a triple-bond structure which may be modified by other factors to be described shortly. The only exceptions to this assumption are the isocyanates where a triple bond apparently is not present.

Cyanides

Relatively few Raman lines have been observed from the inorganic compounds, in spite of the complexity of the ions in some of them. The results that have been obtained for a typical group of both simple and complex cyanides are shown in Table 90.

In most cases only a single line has been noted for the cyanide ion. Quite a few of these determinations have been qualitative rather than quantitative so that not too much importance need be attached either to the intensities of the lines present or to the absence of expected lines. It is noticeable, however, that practically all the Raman shifts for the cyanide grouping are less than those observed in the organic cyanides or nitriles. In some cases the magnitude of the shift occurs in the region of the cyanide shift in the isonitriles. This does not warrant the conclusion that the constitution of the inorganic cyanides is similar to that of the isonitriles. A whole series of Raman shifts occurs near $\Delta\tilde{\nu}$ 2060–2080 in those inorganic cyanides which ionize readily. It would seem that the explanation originally advanced by Dadieu and Kohlrausch⁴³⁸ is probably correct.

Table 90.—The Raman Shifts from Cyanogen Compounds.

Compounds	Raman Shifts				
HCN, gas, at 80° C.					
HCN, liquid					
NaCN, cryst.					
KCN, sol.					(838)
(CN) ₂ , liquid			512	(756)	860
Hg(CN) ₂	260(1)				
Hg(CN) ₂ , cryst.	276				
KAg(CN) ₂	239(2)				855(1)
KCu(CN) ₂					
K ₃ Cu(CN) ₄					
K ₂ Cd(CN) ₄					
K ₂ Fe(CN) ₆ · 3H ₂ O, cryst.					
K ₂ Fe(CN) ₆					
K ₂ Ni(CN) ₄					
K ₂ Ni(CN) ₄ (?)					
K ₂ Hg(CN) ₄					
K ₂ Zn(CN) ₄					
K ₃ Cr(CN) ₆				782(5)	
K ₃ Cr(CN) ₆			619(1)		
K ₃ Co(CN) ₆	340(5)	(405)			
K ₃ Ru(CN) ₆	381				
K ₃ Rh(CN) ₆			593		
NaSCN				754(2)	
KSCN				747(5)	796(0)
KSCN, cryst.				747(5)	
NH ₄ SCN				744(5)	
NH ₄ SCN, cryst.					
KSeCN			575		
Ba(SCN) ₂ , cryst.				776	
KOCN					838(1) 1229(0)
CICN	397(1)			729(5)	
BrCN	368(1)		580(5)		
ICN	321	470(5)			
HCN, gas, at 80° C.		2089(5)			
HCN, liquid	2069(0)	2096(8)	(2122)		3213
NaCN, cryst.		2085(5)			
KCN, sol.		2081(5)		2160(0)	
(CN) ₂ , liquid					2334(1)
Hg(CN) ₂				2196(8)	
Hg(CN) ₂ , cryst.				2192(5)	
KAg(CN) ₂			2130(1)		
KCu(CN) ₂			2110		
K ₃ Cu(CN) ₄		2094(5)		(2176)	
K ₂ Cd(CN) ₄			2142		
K ₂ Fe(CN) ₆ · 3H ₂ O, cryst.			2161		
K ₂ Fe(CN) ₆	2051(5)	2092(5)	2153	2195	
K ₂ Ni(CN) ₄			2144(5)		
K ₂ Ni(CN) ₄ (?)			2142(5)		
K ₂ Hg(CN) ₄			2150(3)		
K ₂ Zn(CN) ₄	(2055)		2149(3)		
K ₃ Cr(CN) ₆			(2137)		
K ₃ Cr(CN) ₆			2130(5)		
K ₃ Co(CN) ₆	(2070)		2141(3)		
K ₃ Ru(CN) ₆	2068(5)		2107(3)		
K ₃ Rh(CN) ₆			2145(3)		
NaSCN	2076(5)				
KSCN	2058(8)				
KSCN, cryst.	2050(8)				
NH ₄ SCN	2066(8)				
NH ₄ SCN, cryst.	2067(5)				
KSeCN	2060				
Ba(SCN) ₂ , cryst.	2053(5)				
KOCN	1314(0)			2183(1)	
CICN					2201(8)
BrCN				2187(8)	
ICN			2158(8)		

The $\Delta\bar{\nu}$ 782 for $K_3Cr(CN)_6$ and $\Delta\bar{\nu}$ 340 for $K_3Co(CN)_6$ have been attributed to the oscillation of the complex.⁴⁶¹ The same might be said of $\Delta\bar{\nu}$ 855, observed in $KAg(CN)_2$. The shift $\Delta\bar{\nu}$ 838 possibly observed in potassium cyanide solution¹²⁰⁸ is doubtful. Otherwise, the shifts appearing near $\Delta\bar{\nu}$ 750 occur exclusively in compounds containing sulfur and are attributed

to the triatomic nature of the ion. Similarly, the shift $\Delta\bar{\nu}$ 838 observed in potassium cyanate¹²⁰³ may be attributed to the triatomic character of the cyanate ion. On occasion, there is present a somewhat curious anomaly, namely, the compounds containing heavy cations have larger frequency shifts than those containing lighter ones. This is diametrically opposed to observations of other compounds, and has been explained by Pal and Sen Gupta¹²⁰⁵ as due to a change in the binding force which is influenced by the electronic configuration surrounding the atom. Krishnamurti⁹¹¹ attributes $\Delta\bar{\nu}$ 260 and 276 in mercuric cyanide (solution or crystal) to the $\text{Hg} \leftrightarrow \text{CN}$ oscillation. He considers the molecule as linear and the binding force as being mainly homopolar. The frequency shift ($\Delta\bar{\nu}$ 2100) increases when there is an increase in the homopolar nature of the $\text{R}-\text{CN}$ binding. The same view is taken by Samuel and Khan.¹⁴⁰³ Volkenshtein¹⁶⁶² has observed the frequencies near $\Delta\bar{\nu}$ 275 and 2190 in crystals and $\Delta\bar{\nu}$ 260 and 2194 in aqueous solution. Ammoniacal solutions cause little alteration.

Thiocyanates

From the considerations enumerated above it is quite apparent that the classic structure of the thiocyanate ion containing two double bonds is incorrect. Langseth, Nielsen and Sørensen⁷⁹¹ have compared the spectra obtained from carbon oxysulfide, thiocyanate ion and chlorocyanide. These show some general similarity. In all three cases three Raman frequencies are observed. In the chapter on the Raman spectra of gases it is pointed out that carbon oxysulfide gives rise to a frequency which is a harmonic of ν_2 . This appears at $\Delta\bar{\nu}$ 1041, and is in addition to the fundamentals corresponding to ν_1 , ν_2 and ν_3 . The oscillation corresponding to ν_2 is absent in the thiocyanate ion. However, ν_1 and ν_3 as well as $2\nu_2$ are present. In the chlorocyanide $2\nu_2$ is absent and ν_2 is present. In this compound the observed frequencies corresponding to ν_1 , ν_2 and ν_3 are, respectively, $\Delta\bar{\nu}$ 729, 397 and 2201. In the thiocyanate ion these frequencies are obviously $\Delta\bar{\nu}$ 750, 398 (unobserved) and 2066. These interpretations are partly confirmed by the polarization observations, which indicate that $\Delta\bar{\nu}$ 720 has a depolarization factor of 0.08 and $\Delta\bar{\nu}$ 2066 a factor corresponding to 0.37. If this interpretation is correct in the case of the thiocyanate ion and chlorocyanide it is the unsymmetrical oscillation which has the greatest intensity. If the molecule is linear, as these results seem to indicate, it probably has the symmetry $\text{C}_{\infty v}$. As has been mentioned before, there is, therefore, no possibility of the isosteric form, $\text{S}=\text{C}=\text{N}^-$, and the constitution of the ion may be adequately described by the formula $\text{N}\equiv\text{C}-\text{S}^-$. The force constant calculated for the $\text{C} \leftrightarrow \text{N}$ grouping is 14.3×10^5 dynes cm^{-1} , and for the $\text{S}-\text{C}$ linkage 5.4×10^5

dynes cm.⁻¹ Kondrat'ev and Setkina⁸⁹¹ have investigated potassium selenocyanate and have obtained two Raman shifts, $\Delta\tilde{\nu}$ 575 and 2051. It is pointed out by these authors that the force constants for C—N and O—H do not change greatly when another electron is added to form CN⁻ or OH⁻. Furthermore, taking into consideration the mass effect, there is not much change in the force constant on the substitution of chlorine, bromine, or iodine to form chlorocyanide or equivalent halogen derivatives. It is to be expected that there would be no appreciable change in the force constant in going from NCS⁻ to NCSe⁻.

The calculated force constant for the seleno- compounds is 14.6×10^5 dynes cm.⁻¹ Spacu¹⁴⁹³ also has investigated the Raman spectra of potassium selenocyanates and has observed a single intense Raman line at $\Delta\tilde{\nu}$ 2074 in fair agreement with the results of Kondrat'ev and Setkina. The lower frequency shift at $\Delta\tilde{\nu}$ 575 was not observed by Spacu. He concludes that the seleno-cyanate ion is similar to the thiocyanate ion already described. Some evidence is offered also to indicate that the selenocyanate ion is isosteric with bromocyanide.

Considering more specifically the halogen derivatives of the cyanides, it is noticed that the C $\leftrightarrow$ N group is affected by the mass of the halogen substituents. This effect, however, extends only over a spread of some 20 wave numbers. In contradistinction to this, the effect of halogen substitution on the ν_1 valence vibrations is to diminish the magnitude of this vibration from $\Delta\tilde{\nu}$ 729 to 470 in going from chlorocyanide to iodocyanide. This is a change of nearly 300 wave numbers. The ν_2 vibration corresponds to the bending motion of the halogen atom in a direction perpendicular to the symmetry axis. The observations of West and Farnsworth¹⁶⁸¹ on the halogen derivatives were made from alcoholic solutions and in the liquid state. It would seem justifiable, nevertheless, to emphasize the similarity between the spectra obtained from chlorocyanide and the thiocyanate ion. In view of the equivalence in mass of the chlorine atom and the sulfur atom and similarity of the magnitude of the shift corresponding to the valence vibration, it can be concluded with some justification that the S $\leftrightarrow$ C vibration is a single-bonded one corresponding to approximately $\Delta\tilde{\nu}$ 750. It will be recalled that this frequency appears in the organic thiocyanates and isothiocyanates between $\Delta\tilde{\nu}$ 630 and 700. In the organic thioethers this appears generally as a doublet at $\Delta\tilde{\nu}$ 735 and 650. In the simpler mercaptans from methyl to butyl mercaptan the C—S linkage varies from $\Delta\tilde{\nu}$ 700 to approximately 650. This is a distinct lowering of this vibration in the organic thiocyanates as compared with the thiocyanate ions. Such a lowering does not seem unreasonable in view of the fact that the triple-bond linkage of the cyanide group is itself affected by ionization in a very definite fashion, as has been pointed out in compar-

ing the Raman shift of the organic nitriles with the inorganic cyanides. The splitting of the Raman shift corresponding to the C—S vibration in the organic sulfur derivatives may be likened to the behavior of a similarly located frequency in dichloromethane as compared with the monohalogen derivatives. Particular emphasis has been placed on a delineation of the relationship of the Raman shift of these compounds to the carbon-sulfur binding because these relationships are distinctly involved in a consideration of the structure of carbon disulfide.

Returning then to a consideration of the large number of other cyanide derivatives, it is apparent that the Raman spectra of cyanogen compounds as recorded in Table 90 are incomplete. The lack of proper intensities and polarization data also is embarrassing in any attempt to delineate the structure of these compounds. If these compounds were completely ionized into cyanide ions and other cations the only shift present would be the one corresponding to the carbon-to-nitrogen linkage. Hence if the low-frequency shift observed is really present, there is incomplete ionization. Furthermore, if one low-frequency shift is present there should be others. The complex cyanide compounds, such as potassium cadmium cyanide, for example, probably do not exist as such in solution. This compound would give rise to 15 Raman lines if there were no degenerate vibrations. No possible degeneracy would account for the absence of all but one line. This is about all that can be said about the complex cyanides on the basis of the information at hand. Rather than indulge in pure speculation, it would seem wiser to await the accumulation of more accurate data before attempting to discuss in detail the constitution of these ions or compounds in solution.

It may be mentioned, however, that hydrogen cyanide may have the symmetry $D_{\infty h}$ and should, therefore, give rise to three observable Raman lines. If the frequency recorded at $\Delta\bar{\nu}$ 3213 for liquid hydrogen cyanide is indeed real, this would indicate that the hydrogen is bound to the carbon atom with a homopolar linkage, and that this frequency corresponds to the H—C vibration in this compound. Mention should also be made of the spectrum observed from potassium cyanate which, according to Pal and Sen Gupta,¹²⁰⁸ has four Raman lines of which one is $\Delta\bar{\nu}$ 2183(1). This is weak in intensity as compared with the other C≡N shift. Nevertheless it is present, in contradistinction to its complete absence in the organic isocyanates. These organic isocyanates have the structure R—C=N=O and consequently are not analogous to the K—O—C≡N structure of potassium cyanate. The lack of adequate data will not permit further comment on the structure of this compound as derivable from Raman spectra data.

Complex Compounds

Complex compounds may exist in the vapor, liquid, or solid states of aggregation or in solution. By the term "complex compounds" is meant those molecules, alike or unlike, which may combine to form double polymers, mixtures, coördinated complexes and quasi-compounds, whose real existence has been more or less questionable. The Raman spectra studies offer in many cases a unique means of determining the existence of certain types of complexes. In true mixtures the Raman spectrum of each compound is approximately independent of the spectra of the other constituents. If, however, there is an actual interaction, the normal Raman spectra will be considerably affected. An early example of this is seen in the polymerization of sulfur trioxide. This has been discussed in detail in the chapter on the Raman spectra of sulfur oxides. In the organic portion of this work the formation of polystyrene from styrene, paraldehyde from acetaldehyde and the methyl methacrylate polymers has been mentioned. These are examples of rather stable compound formation from simple units. An example of unstable compound formation is seen in the interaction of formaldehyde with water in an aqueous solution to produce methylene glycol.⁷²⁷

Proof of the formation of a mixed molecule by use of the Raman effect has been demonstrated by Trumphy.^{1583, 1585} The procedure was first to determine the Raman shift for the pure halides, such as phosphorus trichloride and phosphorus tribromide. These were then mixed in varying ratios and the Raman spectra of the molten mixtures determined. These mixtures give rise to new Raman lines. If these mixtures were "true" mixtures, the Raman lines would be only those attributable to each pure compound and would vary in intensity depending on the proportion of the pure constituents present. However, if there is an interaction between the constituents, new lines will appear which will be characteristic of the particular compounds formed. The phosphorus trichloride and phosphorus tribromide mixtures evidently produce two new molecules having the formulas PCl_2Br and PClBr_2 . Mixtures of silicon tetrabromide and stannic bromide, on the other hand, show no new Raman lines. The system stannic chloride and phosphorus tribromide shows the presence of seven new compounds, namely, SnBr_4 , PCl_3 , PClBr_2 , PCl_2Br , SnCl_3Br , SnCl_2Br_2 and SnClBr_3 . Mixtures of phosphorus trichloride with phosphorus tribromide have also been investigated by Burkard.³⁰⁰ The Raman effect in ten different mixtures of these two compounds was investigated. It was noted that with an increasing concentration of phosphorus trichloride the valence frequency (ν_1) becomes smaller. The compound PCl_2Br , as predicted by Trumphy, was found and its intensity

maximum was in the mixture corresponding to $6\text{PCl}_3\cdot 3\text{PBr}_3$. These results are shown in Figure 72.

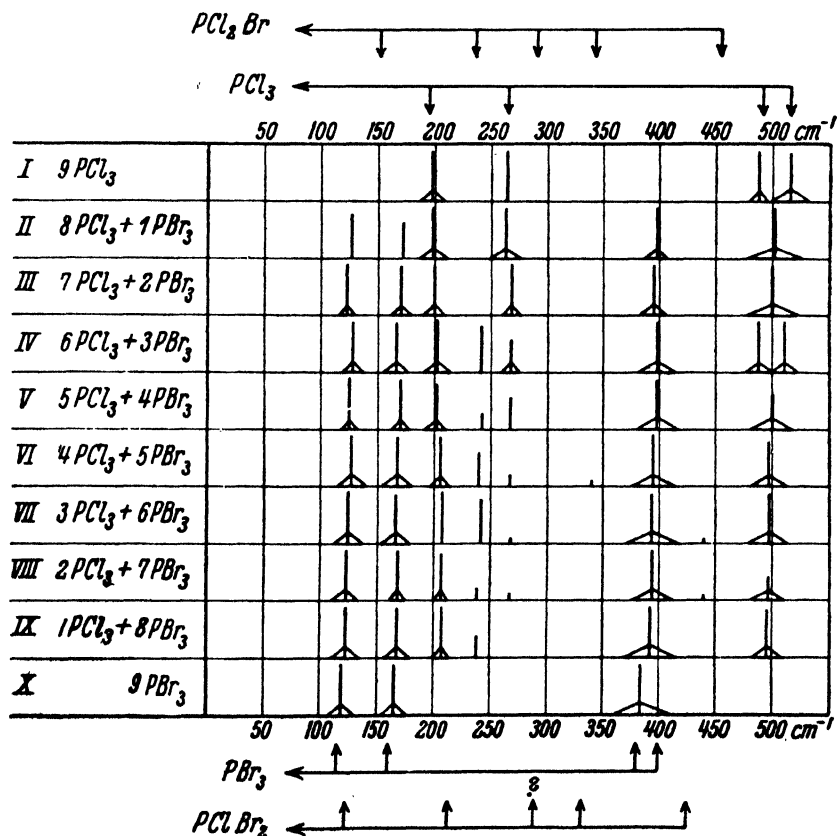


FIGURE 72. The Raman Spectra of Mixtures of Phosphorus Halides (after Burkhard).

Krishnamurti⁹¹⁹ has studied the Raman spectrum of mercuric chloride in the crystalline form. This is found to give a very strong line at $\Delta\tilde{\nu}$ 313 and a faint one at $\Delta\tilde{\nu}$ 381. Mercuric bromide, however, gives only an intense line at $\Delta\tilde{\nu}$ 187. A concentrated solution of mercuric chloride in methyl alcohol gives a single line very much broadened at $\Delta\tilde{\nu}$ 319. Mercuric ammonium chloride was next examined in the powder state and was found to give a single frequency very much shifted from the mercuric chloride line toward a shorter wave-length at $\Delta\tilde{\nu}$ 273. An aqueous solution of this compound gives the same Raman displacement. This modi-

fication of the normal mercuric chloride shift is evidently due to the influence of the ammonium chloride molecule. Mixtures corresponding to one mole of mercuric chloride plus two moles of ammonium chloride in solution give the same spectrum as is obtained from crystalline mercuric ammonium chloride. This would seem to indicate the formation of mercuric ammonium chloride in solution or at least the presence of an HgCl_4 ion. In a solution consisting of a one-to-one molal ratio of mercuric chloride and ammonium chloride two lines appear, one at $\Delta\tilde{\nu}$ 274, medium strong but very broad, and another $\Delta\tilde{\nu}$ 310, very weak. Under these circumstances there is insufficient ammonium chloride to combine with all the mercuric chloride and produce exclusively HgCl_4^{--} . The $\Delta\tilde{\nu}$ 310, therefore, should represent mercuric chloride in solution and probably corresponds to the $\text{Hg} \leftrightarrow \text{Cl}$ oscillation. These results are somewhat similar to those obtained by Braune and Engelbrecht^{275, 276} with solutions of mercuric halides and potassium chloride. The compounds K_2HgBr_4 and K_2HgI_4 yield $\Delta\tilde{\nu}$ 166 and 126 respectively. It is claimed that the principal frequency of the supposed HgX_4 ion has a value which is eight-tenths that of the corresponding shift in the HgX_2 molecules.

Ammoniacal solutions of mercuric cyanide in pyridine and ammonia¹⁶⁵² yield approximately the same results, with minor differences, as do the aqueous solutions.

More recently Bernstein and Martin¹²¹ have studied mixtures of mercuric chloride and hydrochloric acid solutions. As the molecular ratio of hydrochloric acid is increased in proportion to the mercuric chloride present, there is a gradual decrease in the Raman frequency observed at $\Delta\tilde{\nu}$ 315 in a 6-per cent aqueous solution of mercuric chloride containing no acid. The maximum decrease is reached when there are two molecules of hydrochloric acid present for each molecule of mercuric chloride. The minimum frequency is $\Delta\tilde{\nu}$ 265. There is an intermediate concentration range where two measurable Raman frequencies are present, one corresponding to a value slightly greater than $\Delta\tilde{\nu}$ 265 and the other to slightly less than $\Delta\tilde{\nu}$ 302. If the $\Delta\tilde{\nu}$ 265 shift is to be ascribed to the complex H_2HgCl_4 , then this is similar in magnitude to the complex formed by both potassium and ammonium halides. This would seem to be further substantiation of the concept that this frequency originates in the HgCl_4 ion. This reasoning, carried to its logical conclusion, would also suggest that crystalline mercuric ammonium chloride should likewise be ionized.

It should be carefully noted that the mercuric chloride molecule must be both linear and symmetrical to give rise to only one Raman line. It is difficult to conceive under what circumstances two more chlorine atoms could be added to this molecule without changing the symmetry characteristics. It might be argued that the addition of hydrochloric acid caused the

formation of un-ionized HgCl_2 from HgCl ion in solution, and that the diminution in the Raman frequency is caused by the increased mass of one of the vibrating components. There is undoubtedly some common ion effect taking place in a solution of mercuric chloride when the common chloride ion is present. This has been thoroughly demonstrated by Hibben⁷³⁶ in the case of zinc chloride. This is discussed in detail in the portion of this work devoted to inorganic halides as there is no complex compound formation involved in this process.

With zinc chloride and the organic alcohols some compound formation is apparently involved. Hibben⁷²⁸ has shown that, in methyl alcohol solutions of zinc chloride, not only the zinc chloride lines but also several of the alcohol lines are affected. The zinc chloride spectrum is increased in both ethyl and methyl alcohol as far as the principal Raman shift is concerned. In ethyl alcohol the single line becomes a doublet. Whether in the last analysis these observations may be attributed to a compound formation between alcohol and zinc chloride is still open to further investigation.

Three frequencies have been observed⁴⁷³ from zinc iodide solutions, namely, $\Delta\bar{\nu}$ 106(5), 126(8) and 150(5). It is presumed that the first two of these represent a complex ion and the last one represents un-ionized zinc iodide. This concept is predicated on the fact that the presence of alkali iodides increases the intensities of $\Delta\bar{\nu}$ 106 and 126 while a non-ionizing solvent tends to enhance the intensity of $\Delta\bar{\nu}$ 152. (See also Chapter 23 for another discussion of these compounds.)

Cadmium iodide has been the subject of some interesting investigations in connection with complex compound formation, by Venkateswaran¹⁶²² and Delwaulle, Francois and Wiemann,⁴⁷³ although Braune and Engelbrecht^{275, 276} observed no Raman lines from KCdCl_3 and KAgI_2 . In a recent publication (1939) Delwaulle, Francois and Wiemann have apparently quite clearly demonstrated the presence of complex cadmium iodide ions in solution. It was noted first of all that $\Delta\bar{\nu}$ 123(5) and 142(10) ($\rho \approx 0.15$) are present when cadmium iodide is dissolved in non-ionizing solvents. The strongly polarized line is assigned to the linear valence vibration of the un-ionized halide. The other line is presumed to originate in an unknown complex containing less iodine than CdI_4^{--} . However, in an aqueous solution containing no added alkali iodide or in aqueous or alcohol solutions containing added alkali iodide, there is a complete change in the Raman spectra which may be described by the following: $\nu_1 = \Delta\bar{\nu}$ 116 (6.7) ($\rho \approx 0.10$) (the decimal intensities originate from a modification of the reported intensities to a scale of ten), $\nu_2 = \Delta\bar{\nu}$ 36 (8.7) (6/7), $\nu_3 = \Delta\bar{\nu}$ 144(1) (>0.7) and $\nu_4 = 44$ (10) (6/7). The number of shifts and their polarizations are in accord with the suggested formation of a tetrahedral CdI_4

ion. The shift at $\Delta\bar{\nu}$ 144 is entirely different from that occurring at 142 in the CdI_2 molecules. The nondegenerate valence vibration has probably been shifted from 142 to 116 when the complex ion is formed.

Compounds of hydrochloric and hydrobromic acids with alcohols and ethers, investigated by Briegleb and Lauppe,^{280, 281, 282} are discussed under oxonium compounds in the organic section. Tin tetrachloride complexes are mentioned in the section on halides of this type. Briefly, however, it may be stated that the tin halides show a strong modification in their spectra as a result of solution in alcohol or ether. This effect is least in dimethyl ether and greatest in trichloroethane. In tin tetrachloride solutions, for example, the shifts $\Delta\bar{\nu}$ 104(8), 131(5), 371(10), 407(7) are altered in alcoholic solutions to $\Delta\bar{\nu}$ 161, 218, 296, 334(10), 405(2) and 497(2). The ether solutions of aluminum chloride yield possibly $\Delta\bar{\nu}$ 310, and other lines whose frequencies are not too clear, as well as a modification of the normal spectrum from the ether.

Goubeau⁶³⁶ has noted changes in the spectra from alcohol, acetone and dimethyl ether as a result of the interaction between these compounds and a number of perchlorates, and Volkenshtein¹⁶⁵¹ has noted a displacement of the frequencies of dimethyl ether when sulfur dioxide is dissolved in it. Solutions of antimony trichloride in benzene, according to Finkel'shtein, show new Raman lines at $\Delta\bar{\nu}$ 477 and 1236, while diethyl ether solutions of arsenic and antimony halides give no indication of either new compounds or a displacement of known Raman lines.

The next complexes to consider are those derived from ammonia, *i. e.*, the ammino compounds, and their chemical analogs. In this connection it is worth while to mention the work of Joos and Damaschun⁷⁸⁴ and Damaschun,⁴⁵¹ who state that freshly made $\text{Zn}(\text{NH}_3)_6\text{Cl}_2$ gives $\Delta\bar{\nu}$ 418, and that the compound of the composition $(\text{NH}_4)_4(\text{ZnCl}_6)$ yields $\Delta\bar{\nu}$ 274. This shift is attributed by Damaschun to the anion $(\text{ZnCl}_6)^{--}$. However, this can be written as $\text{ZnCl}_2 \cdot 4\text{NH}_4\text{Cl}$ where $\Delta\bar{\nu}$ 274 may be attributed to the spectrum of zinc chloride. In hexammine zinc sulfate there appears $\Delta\bar{\nu}$ 428 which diminishes in intensity if the compound is allowed to stand over a period of time. The presumption is that there is a slow conversion of the hexammino- compounds to tetrammino- compounds under these circumstances. Two of the sulfate lines were observed in the complex compounds, namely, $\Delta\bar{\nu}$ 979 and 1111. In the hexammino-nickel halide derivatives no shift attributable to the complex was observed. The same is true of the diammino- derivatives of silver chloride. Joos and Damaschun argue that there exists a certain similarity between the hydrated salts and the ammino- compounds. To verify this, comparison was made between aquo- compounds and the ammino- compound by the analysis of characteristic oscillations. In none of the salts investigated—where the

Table 91.—Characteristic Raman Shifts of Amino and Allied Compounds.

Compounds	Raman Shifts	Shifts from the Ammonia Group
NH_3		
$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$	410	3223 3306 3394
$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$		
$[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$	419	3305
$[\text{Ni}(\text{NH}_3)_4]\text{Cl}_2$		3309
$[\text{Zn}(\text{NH}_3)_4]\text{Cl}_2$	418	3286 3374
$[\text{Zn}(\text{NH}_3)_2]\text{SO}_4$	428	3183 3274
$[\text{Cd}(\text{NH}_3)_4]\text{Cl}_2$		3193 3268
$[\text{Co}(\text{NH}_3)_4]\text{Cl}_2$		3278 3372
$[\text{Co}(\text{NH}_3)_5]\text{Cl}$	568	
$[\text{Co}(\text{NH}_3)_4]\text{Cl}_2$	482	
$[\text{Co}(\text{NH}_3)_4]\text{Cl}_2$	505(8)	
$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$	390(2)	
$[\text{Rh}(\text{NH}_3)_4]\text{Cl}_2$	475(8)	
$[\text{Pt}(\text{NH}_3)_2\text{Py}_2]\text{Cl}_2$ <i>cis</i>		1015
$[\text{Pt}(\text{NH}_3)_2\text{Py}_2]\text{Cl}_2$ <i>trans</i>		1015
$[\text{PtPy}_2\text{Cl}_2]$ <i>cis</i>		653
$[\text{PtPy}_2\text{Cl}_2]$ <i>trans</i>		653
$[\text{Co en}_3(\text{NO}_2)_2\text{NO}_3]$ <i>cis</i>		
$[\text{Co en}_3(\text{NO}_2)_2\text{NO}_3]$ <i>trans</i>		
$[\text{Co en}_3(\text{SCN})_2]\text{SCN}$ <i>cis</i>	No shifts	1962 2092
$[\text{Co en}_3(\text{SCN})_2]\text{SCN}$ <i>trans</i>	No shifts	1962 2092
$[\text{Pt en}_3]\text{Cl}_2$	225(4)	
$[\text{Pt en}_3]\text{Cl}_2$	250(8)	
$[\text{Rh en}_3]\text{Cl}_2$	219(5)	
$[\text{Ir en}_3]\text{Br}_2$	250?	
$[\text{Zn en}_3]\text{Cl}_2$		
$[\text{Ni en}_3]\text{Cl}_2$		
	960(0)	
	1000	
	996	
	990?	
	997	
	525(8)	
	550(10)	
	439	
	388(0)	
	398(0)	
	571(1)	
	560(1)	
	571(1)	
	398(0)	
	560(2)	
	568	
	568	
	505(8)	
	475(8)	
	390(2)	
	410	
	419	
	418	
	428	
	340	
	No shifts	
	482	
	568	
	568	
	505(8)	
	390(2)	
	475(8)	
	560(2)	
	1015	
	1015	
	653	
	653	
	1962	
	2092	
	1962	
	2092	
	3363	
	3431	
	3364	
	3430	

*Py stands for pyridine and en for ethylenediamine, whose Raman shifts are not included in the table. The ammonia shifts are incomplete.

existence of a definite hydrate is assumed—could a Raman line be detected corresponding to the aquo- compounds. The observed results are included in Table 91. Bose and Datta²⁶⁰ have measured the Raman spectrum obtainable from complex copper compounds. The compounds $[\text{Cu}(\text{NH}_3)_6]\text{Cl}$ Cl_3 and $[\text{Cu}(\text{NH}_3)_6]\text{Cl}_3$ give a modified line at approximately $\Delta\tilde{\nu}$ 568. The compound $[\text{Cu}(\text{NH}_3)_6]\text{Cl}_2$ gives no modified lines. None of these spectra are complete. Spacu¹⁴⁹⁴ has also examined a number of platinum and cobalt complexes of ammonia, pyridine and ethylenediamine. The observed Raman shifts that are attributable to the complexes are included in the previous table. Mathieu^{1035, 1036} has examined $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ and $[\text{Pt en}_3]\text{Cl}_2$ (square configuration), and $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Pt en}_3]\text{Cl}_4$ (octahedral).^{*} There is no difference between these square and octahedral molecules as far as their observed Raman spectra are concerned. The complex compounds $[\text{Rh en}_3]\text{Cl}_3$, $[\text{Ir en}_3]\text{Br}_3$, $[\text{Zn en}_3]\text{Cl}_2$ and $[\text{Ni en}_3]\text{Cl}_2$ were also investigated by Mathieu.¹⁰³⁶ There are from three to four Raman lines between $\Delta\tilde{\nu}$ 200 and 1000 whose origin is in the complex and not in the ethylenediamine. Freymann and Mathieu have also investigated the chloro-platinum derivatives of ammonia and pyridine and conclude that N—H frequency disappears when the nitrogen atom possesses a coördinance of four. This is not compatible with the results that were described previously in the case of ammonium compounds and amines.

A number of complexes formed by the combination of sodium oxide with either molybdenum oxide or tungsten oxide have been investigated. These results are shown in Table 92.

Table 92.—Some Raman Shifts from Tungsten and Molybdenum Complexes.

Compounds	Raman Shifts						
	241(0)	314(2)		843(2)	896(4)	937(4)	
Na_2MoO_4					886(2)		
$\text{Na}_4\text{Mo}_3\text{O}_{11}$					913(2)		959(4)
$\text{Na}_6\text{Mo}_5\text{O}_{21}$							953(4)
$\text{Na}_{10}\text{Mo}_7\text{O}_{41}$							
$(\text{NH}_4)_3\text{MoO}_4$	218(1)	356(1)			890(3)	945(4)	
Na_2WO_4		321(2)	452(0)	832(3)		934(3)	
$\text{Na}_6\text{W}_6\text{O}_{21}$							961

The spectra of the complexes of molybdenum and tungsten have been determined by Damaschun.⁴⁶¹ The spectra of sodium tungstate and sodium molybdate are included for the sake of comparison. There is an apparent increase in the magnitude of the principal Raman shifts with an increase in the complexity of molecular aggregation. Whether these compounds have the formulas assigned to them is another question. Certainly the number of lines which have been obtained so far does not correspond to molecules of the size indicated by the formulas. Theodo-

^{*}In these formulas "en" indicates ethylenediamine.

resco^{1553, 1554} has examined the tungstotartaric complex, obtained by dissolving equal amounts of tartaric acid and sodium tungstate in water. The spectrum of tartaric acid is considerably modified by the presence of sodium tungstate. In particular the carbonyl shift which appears near $\Delta\tilde{\nu}$ 1730 in tartaric acid is diminished to approximately $\Delta\tilde{\nu}$ 1606 in the complex compounds. The molybdotartaric complex is formed in a similar manner and also shows a modification of the carbonyl frequency of the tartrate radical. It will be remembered, however, that the formation of any salt of an organic acid will modify the carbonyl shift of that acid. While these results are indicative of a strong interaction between the molybdate and tungstate compounds with tartaric acid, they are not sufficient to give complete evidence in regard to the constitution of the entire complex. The spectrum of sodium molybdate is but little altered by the formation of the complex. Indeed it is interesting that the spectra of sodium molybdate and sodium tungstate are so very much alike in view of the difference in mass. This indicates that the force constants do not vary widely. Furthermore, the spatial arrangements of the molybdate and tungstate groups are also probably identical. The spectra of the tungstates and molybdates were also mentioned in Chapter 27.

If hydrogen titanochloride may be considered as a complex compound, it might be mentioned that Rumpf¹³⁹⁰ observed that a hydrochloric acid solution of titanium tetrachloride gave rise to a different spectrum from that of pure titanium chloride. Three new frequencies appear, namely, $\Delta\tilde{\nu}$ 251, 340, and 463. These have replaced the observed Raman shift in the original titanium salt and lie at the slightly displaced value between the two groups of paired lines of the tetrachloride salts. The third frequency lies between the two lines $\Delta\tilde{\nu}$ 386 and $\Delta\tilde{\nu}$ 497 observed in titanium tetrachloride. It should not be forgotten, however, that even the symmetrical titanium tetrachloride having the symmetry T_d gives rise to four Raman frequencies, three of which are multiply degenerate. If the compound H_2TiCl_6 gives rise to only three Raman lines, its symmetry must be very great. This would be possible in an octahedral model which has six fundamental vibrations and three active Raman frequencies.

Another series of complex compounds is that originating from silicic acid. A number of the silicic acid esters have been studied. These, however, together with glasses of varying compositions, are treated separately (Chapter 26), as the number of investigations and the importance of this group require a more detailed treatment.

It has been attempted in this discussion to treat in only moderate detail a variety of compounds which give rise to complex mixtures.

Chapter 29

The Raman Spectra of Ammonium Compounds

The Raman spectra of ammonium compounds have been reserved for final consideration principally because they do not fit into the general scheme of molecular types. Furthermore, with the exception of complex ammonium compounds, the shifts attributable to the ammonium ions have been deleted in reporting the spectra of these compounds. This has been done in order to avoid unnecessary confusion. The spectra obtained from ammonia in various states of aggregation have been reported previously in the Raman spectra of gases (Part III) and also in Part II, where the shifts obtained from ammonia, hydrazine and its derivatives were discussed. While it may properly be considered that hydrazine is an inorganic rather than an organic compound, this substance was dealt with in the organic section primarily because of its relation to the organic compounds containing nitrogen.

It will be recalled that gaseous ammonia yields the following shifts: $\Delta\tilde{\nu}$ 943(3) (P), 964(4) (P), 1630(1) (D), 3220(3), 3310(6) (P) and 3380(3), and that, in liquid ammonia, these become 1070, 1585, 3210, 3310 and 3380. It was found from investigation of the hydrazines that if the nitrogen-containing group was charged, the $\overset{+}{\text{N}}\text{—H}$ shifts were diminished to values whose maxima were usually less than $\Delta\tilde{\nu}$ 3200.

For the ammonium ion one would expect a change from the pyramidal symmetry C_{3v} of ammonia to the tetrahedral one T_d . This has been generally accepted by the earlier workers and others who have investigated ammonium salts^{1223, 1320} and more recently by Menzies and Mills.¹⁰⁸⁵ Holmes,⁷⁵³ however, finds that a single crystal of ammonium chloride departs in behavior from the usual tetrahedral structure. More recently Ananthakrishnan^{35, 36} has investigated crystals of ammonium fluoride, chloride, bromide and iodide with the results shown in Table 93.

With the exception of ammonium fluoride and two lines in ammonium chloride, these results agree with the observations of others. Holmes claims to have obtained two lines at $\Delta\tilde{\nu}$ 3232 and 3303, but Ananthakrishnan believes these are due to an incorrect assignment in exciting radiation. Two weak lines appearing near $\Delta\tilde{\nu}$ 3460 and 3545 from $\text{NH}_4\text{NO}_3 \cdot 2\text{NH}_3$ are assigned by Costeanu to the vibrations of the ammonium ion. The presence of $\Delta\tilde{\nu}$ 3160 is further confirmed by the observations of Freymann

Table 93.—The Raman Shifts from Some Ammonium Halides.

Compounds	Raman Shifts					
	2262(0)		2820–2870(3)		3088(2)	3100(2)
NH ₄ F						
NH ₄ Cl	1398(1)	1424(0)	1700(3)	1750(1)	2009(1)	2813(3)
ND ₄ Cl						3040(8)
NH ₄ Br						3142(5)
NH ₄ I	1065(1)		1215(0)		2113(2)–2114(1)	2214(6)
(NH ₄) ₂ SO ₄	1395(1)		1690(6)	2000(0)	2800(3)	2346(6)
(Incomplete)			[1662(0)]*		2780(0)	3025(8)
						[3021(6)]
						3100(4)
						3160(0)

*The shifts in brackets occur with any intensity only at low temperatures.

and Freymann (Raman Jubilee volume)—and these same workers in collaboration with Yeou Ta—who have investigated ammonium nitrate in the crystalline and molten states and in solutions of various concentrations. It is noted that $\Delta\tilde{\nu}$ 1411–1455 observed in solution diminishes in intensity and finally disappears as dilution increases.

There is, therefore, little similarity between the ammonia and ammonium spectra. At the same time there are some noticeable differences among the spectra of the ammonium ion in the above salts. In ammonium iodide, for example, there is only one broad line at $\Delta\tilde{\nu}$ 3100 in place of two separate ones. Some of the frequencies that appear to be absent were simply not observed.

It should be pointed out that, at room temperature, ammonium chloride and bromide both possess the body-centered cube crystal structure, while ammonium iodide at room temperature is of the rock salt type. Furthermore, at low temperatures the ammonium iodide lattice changes over to the ammonium chloride and bromide type, while at high temperatures these two halogens change over to the ammonium iodide type. This is important in the sense that crystal structure has been shown to modify Raman shifts (cf. calcite and aragonite). The appearance or strengthening of the lines in ammonium iodide at $\Delta\tilde{\nu}$ 1662 and 3021, when the iodide has the same crystal structure as the chloride and bromide is therefore explained. Ammonium fluoride belongs to the hexagonal system and does not exhibit polymorphism.

Menzies and Mills assume that part of the results obtained by them at different temperatures is attributable to the rotation of the ammonium ion in the crystal lattice above approximately -30° , at which temperature the lattice vibration $\Delta\tilde{\nu}$ 160–180 disappears. If the tetrahedral model is assumed, it is possible that the following shifts, $\Delta\tilde{\nu}$ 1403, 1712, 3043 and 3123, correspond to the ν_4 , ν_2 , ν_1 , ν_3 types of vibration, as in methane. This seems a reasonable assignment but it leaves unexplained the shifts at $\Delta\tilde{\nu}$ 2000 and 2800, and the fact that all of these lines are active in the infrared. As Ananthakrishnan has suggested, $\Delta\tilde{\nu}$ 2800 may be a harmonic of $\Delta\tilde{\nu}$ 1400, or it may be the result of an accidental degeneracy arising from the interaction of $\nu_4 + \nu_2$ with ν_3 splitting $\Delta\tilde{\nu}$ 3123 into two components. As far

as the appearance of all these lines in infrared absorption and Raman spectra is concerned it is to be remembered that the ammonium ion is a charged group, in comparison with methane, which is completely neutral, and that the presence of the negatively charged anion must alter the force fields in the vicinity of the ammonium ion. This is shown by the splitting of the ν_4 triply degenerate type of vibration, and the ν_2 doubly degenerate types into separate components in ammonium chloride. This splitting is possibly the result of a tendency toward a less regular tetrahedral structure and has been observed to take place, for example, under the influence of water of crystallization.

Ammonium chloride- d_4 gives Raman shifts in position roughly corresponding to the relation:

$$\Delta\tilde{\nu}_{ND_4} \times \sqrt{2} = \Delta\tilde{\nu}_{NH_4}$$

There are some slight differences, namely, the $\Delta\tilde{\nu}$ 2009 shift from ammonium ion is absent and $\Delta\tilde{\nu}$ 2813 is split into two components in ND_4 . The mean of these components still corresponds, however, to $2\nu_4$.

The purport of all the evidence seems to be in the direction that the ammonium ion is a slightly distorted tetrahedron and that the observed Raman shifts are slightly influenced by temperature, crystal structure and the anion. There is one exception concerning the proper appearance of lines due to the ammonium ion, that is, when ammonium salts are dissolved in liquid ammonia. Volkenshtein ¹⁶⁵⁰ has observed that with nitrates and thiocyanates the shifts corresponding to these ions were normal but that lines characteristic of the ammonium group were not observed. This is explained as due to the formation of $[H(NH_3)_n]^+$.

The specific heat of ammonium chloride has been calculated with the aid of Raman spectra data by Sirkar and Gupta.

Afterword

The object of this book has been to give the theoretical background of the Raman effect, to describe the various experimental methods employed, to demonstrate its multitudinous applications to all branches of the physical sciences and to analyze critically and interpret the results of more than a decade of experimentation. In addition, the literature references of each author and a list of publications concerning each chemical compound investigated are made available in convenient form. The method of presentation has, in general, been one of proceeding from the simple to the more complex, thus enabling the reader who is completely unfamiliar with Raman spectra to acquire the back-log of information and vocabulary which is indispensable to a proper understanding of this subject. The division of the book into three main parts and the segregation of subject matter into specific chapters has been for the purpose of allowing the reader to pursue more easily any preferred phase of the subject. It is hoped, therefore that this book will be of assistance to those now working in this field, that it will awaken an interest in those who are not and that it will encourage the use of Raman spectra in solving some of the problems which confront all scientific investigators.

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No special mention has been made in Chapters 3 to 6 of the contributions of other authors to the ideas expressed therein. This is because the material presented represents rather a consensus of opinion than the exclusive contributions of individual authors. When a theoretical paper contains experimental data a discussion of the theoretical implications is usually to be found somewhere in the text. Cases may arise, however, in which a paper concerned almost exclusively with theory is not referred to elsewhere than in the bibliography. It was thought advisable, therefore, to indicate separately the authors who have contributed in a large measure to the theoretical aspects of the Raman effect. This procedure is not too satisfactory as it has been difficult at times to differentiate between theoretical and experimental contributions. The literature references of these authors may be found in the bibliography by means of their special numerical designation—italicized reference numbers. This approximate classification of articles according to theoretical emphasis may be further limited by specifically mentioning those authors who have, in general, provided the background upon which is predicated the theoretical treatment of this volume. These are Andrews, Bhagavantam, Cabannes, Daure, Dennison, Kohlrausch, Mulliken, Manneback, Mecke, Placzek, Radakovic, Raman, Rasetti, Redlich, Rosenthal, Sirkar, Sutherland, Teller, Trumpy, Van Vleck, Venkateswaran, Weiler and Wilson.

In addition to the papers of these authors there are a number of publications to which special attention should be drawn. These include other bibliographies, tables and reviews which cover in detail at least some important aspects of the Raman effect. Reviews of limited length are listed in two publications by Hibben.^{720, 732} The latter publications not only include author bibliographies but also indices of various compounds. The other, shorter publications are as follows:

Bhagavantam,¹²⁹ Ganesan,⁵⁷² Magat,¹⁰¹⁰ Placzek,¹²⁴⁶ Sirkar and Chakravarty,¹⁴⁷⁴ Spomer,¹⁵⁰¹ Weiler.¹⁶⁷³

At the present time there are four books of varying degrees of completeness on the subject of Raman spectra. These are by Kohlrausch,⁸¹⁹ Daure⁴⁶¹ and Sutherland.¹⁵²⁵ In addition there will appear shortly a new book by E. Bright Wilson, Jr., and Paul C. Cross to which special attention is called as it deals with the theoretical aspects of the Raman effect.

In the following alphabetical list of authors it has been attempted to include all publications from the discovery of the Raman effect up to

the fall of 1938. Immediately following this alphabetical list is given a supplementary list of authors without reference numbers. In the latter are included: (a) those publications, by the same authors, which have been superseded by more recent or more detailed material of approximately the same context; (b) those publications which were inadvertently overlooked; (c) those which have appeared while this book was being printed.

The significant information obtainable from these publications usually has been embodied in the text. In these cases no reference number is available but the source of the original material may be found by consulting the names in the supplementary bibliography. Current literature appearing up to approximately June, 1939 is included.

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Indices of Compounds

Introduction

In view of the previous publications of the author and others (already referred to in the bibliography) who have tabulated some of the compounds investigated together with their constitutional formulas, it does not seem advisable or necessary to repeat these formulas in this book. However, a list of all the organic and inorganic compounds that have been investigated thus far—together with a means of ascertaining the original source of information—is undoubtedly of considerable value to those interested in this field, and it is felt that the usefulness of this book is much extended thereby.

The various classes of compounds are referred to in the text together with sufficiently abundant references to satisfy all ordinary requirements. The compounds in the indices, therefore, are not subdivided into classes or by formula but are listed alphabetically by name. This raises the question not only as to general systems of nomenclature but also, occasionally, the question of naming individual compounds. In general the system adopted follows as closely as possible that employed by *Chemical Abstracts*, but in discussing such compounds as the terpenes, for example, it has seemed more desirable to use the common names rather than to employ the Geneva system. Other compounds which may be named in several ways are listed, in general, under both the common name and the more correct one in the indices.

The indices consist of two portions, listed separately. The first contains the inorganic, and the second the organic, compounds. With few exceptions the organic compounds are considered to be those which contain both carbon and hydrogen. Carbon tetrachloride, for example, is dealt with in the organic section and carbon disulfide in the inorganic because this arrangement places each of these compounds with those to which it is more closely related. In the inorganic division the great majority of compounds are listed alphabetically according to the manner in which their formulas or common usage indicate. The salts of phosphorous, phosphoric, arsenious and arsenic acids, however, are indexed under phosphites, phosphates, **arsenites** and **arsenates**. This has been done because there is no generally accepted nomenclature for these compounds, and because it is the anions or complex groups which are principally of interest from the point of view

of Raman spectra. The co-ordination compounds are named according to the Werner system of nomenclature and are so indexed.

Each of the names of these compounds is followed by a number or numbers, under which the author and reference may be found in the bibliography. When an author publishes the same article in more than one journal, as for example many of the publications of Kohlrausch and his associates, both references are given in the compound index and bibliography.

In addition there is a numerical index giving the page in this volume upon which reference is made to any compound or to the work of any author.

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